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# Polymer-Assisted Deposition (PAD) and Its Applications

**Quanxi Jia**

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Los Alamos National Laboratory
Los Alamos, NM 87545

**LA-UR-14-22920**

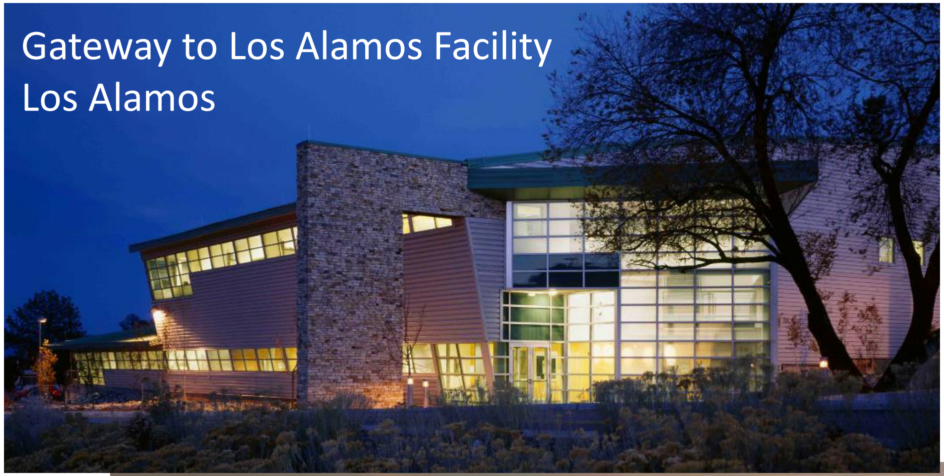
# DOE National Laboratories


U.S. DEPARTMENT OF ENERGY

# BES Nanoscale Science Research Centers (NSRCs)

# Center for Integrated Nanotechnologies

**CINT**: A DOE User Facility for nanoscience research at
*Los Alamos and Sandia National Laboratories*


Gateway to Los Alamos Facility
Los Alamos

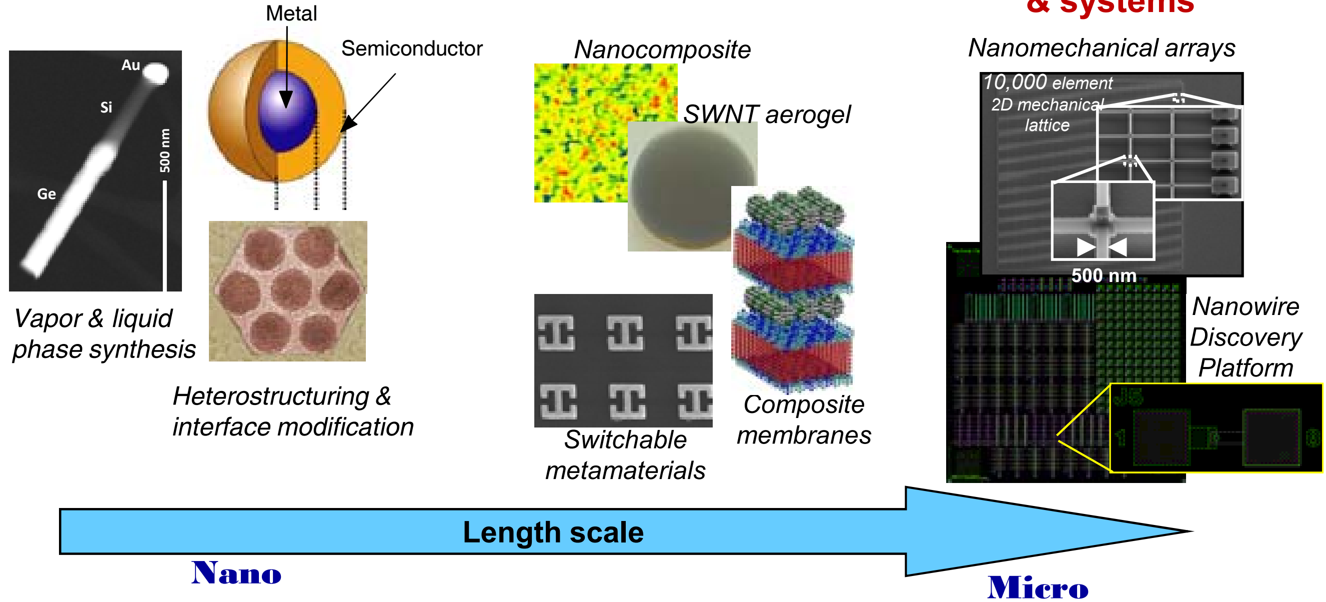
- **New Science**
- **New Tools**
- **Innovative approaches to nanoscale integration**


Core Facility, Sandia National Laboratories Albuquerque

# The CINT Vision & Mission

***One scientific community focused on nanoscience integration***

**Nanoscale building blocks** | **Fabrication & assembly** | **Functional composites & systems**



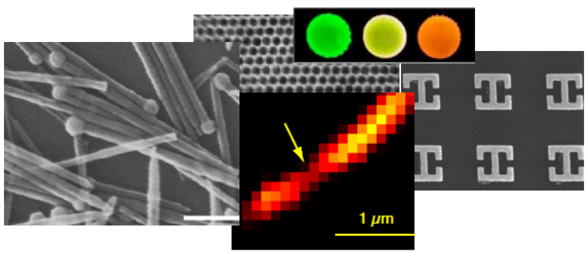

**Establishing the fundamental principles that underpin the integration of nanomaterials is of paramount importance to nanoscience and ultimately nanotechnology.**

Los Alamos NATIONAL LABORATORY | U.S. DEPARTMENT OF ENERGY | Office of Science | Sandia National Laboratories

# Science Thrusts: The Foundation of Our Science and User Programs

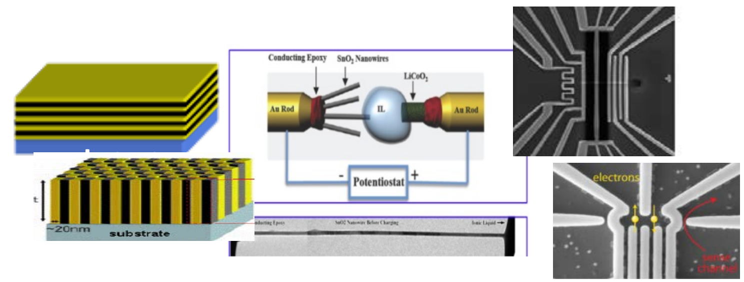
## Nanophotonics & Optical Nanomaterials (NPON)

Synthesis, excitation and energy transformations of optically active nanomaterials



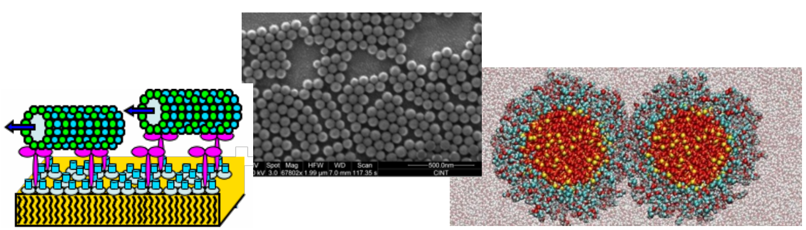

## Nanoscale Electronics & Mechanics (NEM)

Control of electronic transport, wavefunction, and mechanical coupling using nanomaterials



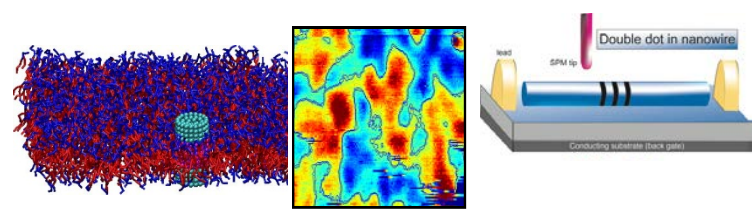

## Soft, Biological, & Composite Nanomaterials (SBCN)

Solution-based nanomaterials synthesis and assembly of soft, composite  and artificial biomimetic nanosystems



## Theory & Simulation of Nanoscale Phenomena (TSNP)

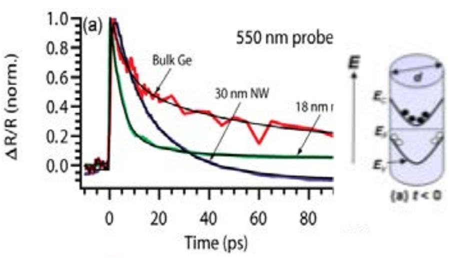
Assembly, interfacial interactions, and emergent properties of nanoscale systems



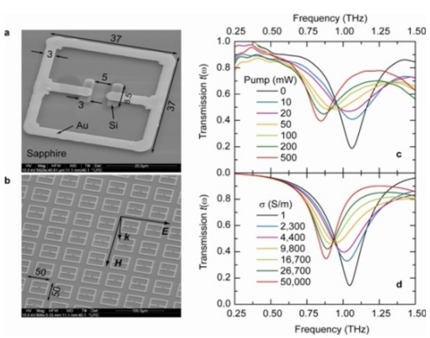
# CINT Special Strengths

## Ultrafast photonics

### Carrier Dynamics



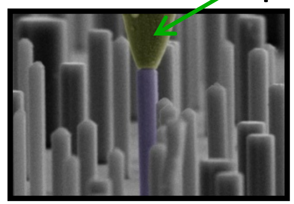

### THz Metamaterials



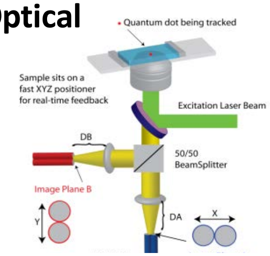

## Nano-manipulation & scanning probes

### Electrical

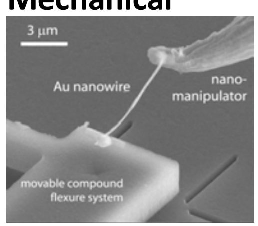
Conducting probe



### Optical



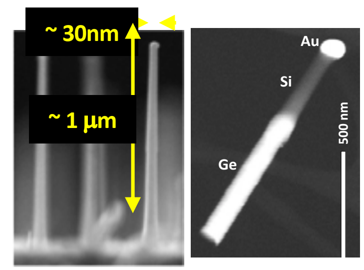

### Mechanical



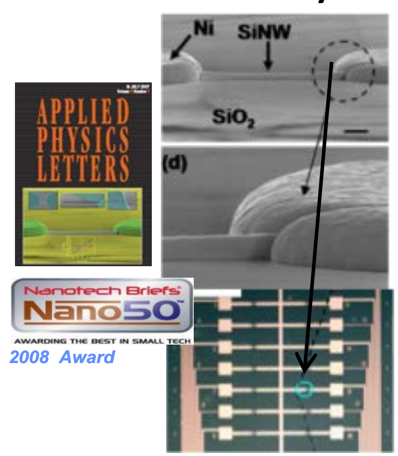

CINT user C. Volkert

## Nanofabrication

### Synthesis



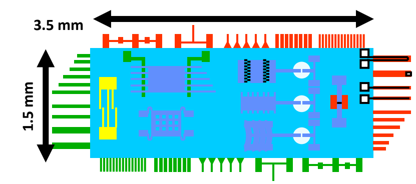

### Directed Assembly



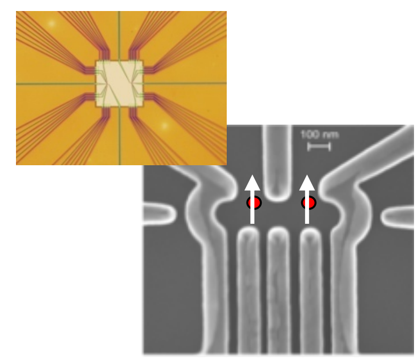

## Discovery Platforms™

(Microsystems to interrogate nanomaterials)

### Cantilever Array platform




### Quantum Computing Transport platform



# Acknowledgements

**Y. Lin, P. Shukla, M. Jain, H. Luo, G. Zou, S. A. Baily, Y. Y. Zhang, N. Haberkorn, G. Collis, F. Ronning, A. Mueller, N. A. Mara, L. A. Civale, A. K. Burrell, T. M. McCleskey, E. Bauer, and M. E. Hawley**

Los Alamos National Laboratory, Los Alamos, NM 87545

**J. H. Lee, L. Chen, C. Y. Chou, Z. Bi, X. H. Zhang, and H. Wang**

Texas A&M University, College Station, TX 77843

# Outline

- Introduction
- Experimental details and results
  - Metal-oxide films
  - Metal-nitride films
  - Metal-carbide films
  - Other coatings
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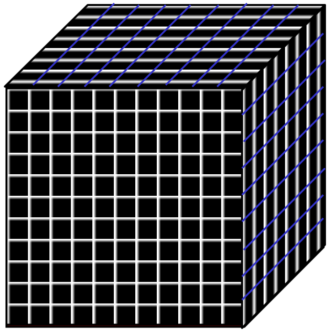
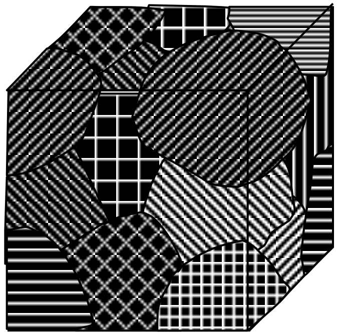
# Flexibility of Thin Films: Architectures and Functionalities

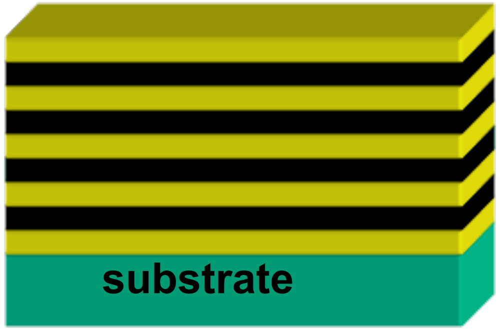
- Single crystals
  - ✓ Intrinsic properties
  - – Control, size, and availability

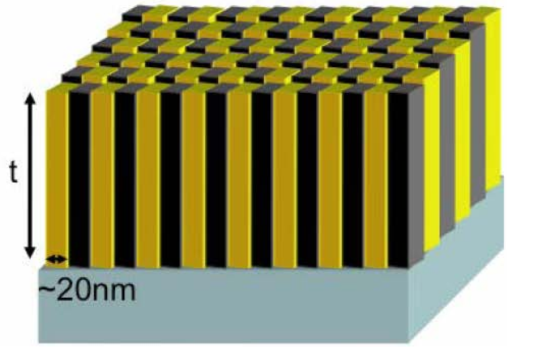


- Ceramics
  - ✓ Easy process
  - – Grain boundaries & impurities

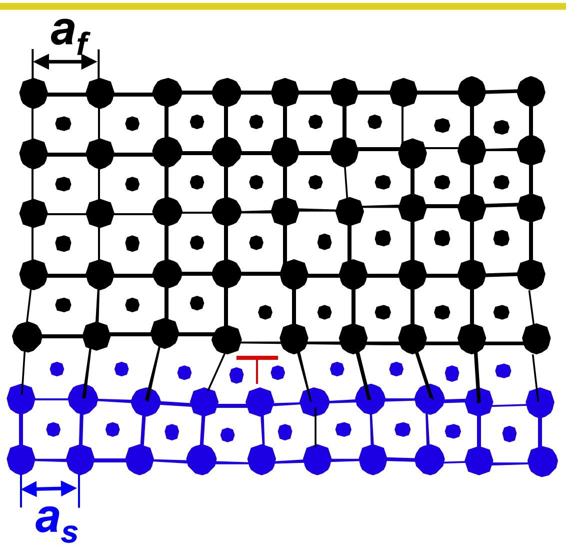


- Thin films
  - ✓ Artificial architectures and microstructures
  - ✓ Controlled dimensionalities
  - ✓ Growth at far-from or near equilibrium conditions
    - Metastable phases
    - Lattice strain
    - Anisotropy
  - – Complexities



# Advantages of Epitaxial Thin Films




$$f = \frac{(a_f - a_s)}{(a_f + a_s)/2} \approx \frac{a_f - a_s}{a_s}$$

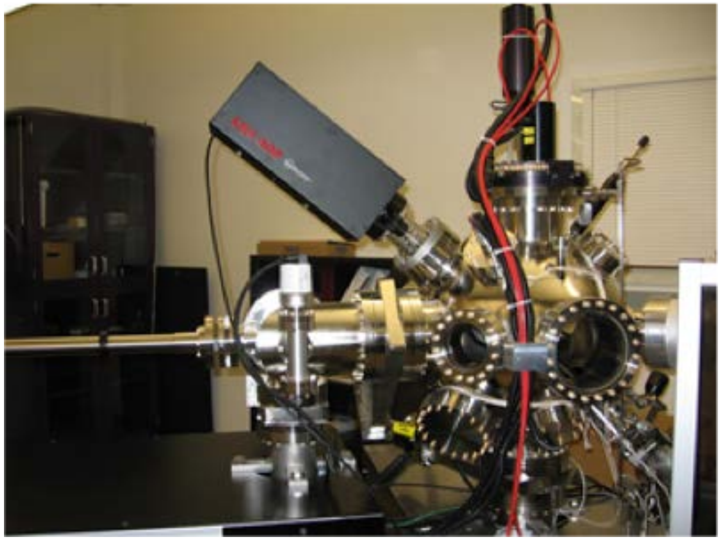
- When the lattice mismatch is large, strain can be partially relaxed through misfit dislocations.
- When the lattice mismatch is small, the film can be strained.

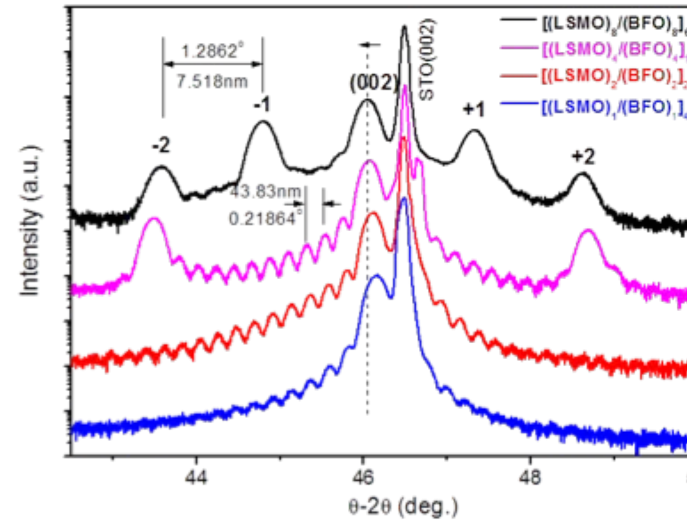
- Single-crystal not available
- Grainboundary in polycrystalline films
- Locking-in the crystal structure, and so the phases
- Induced preferential orientation
- Well controlled properties

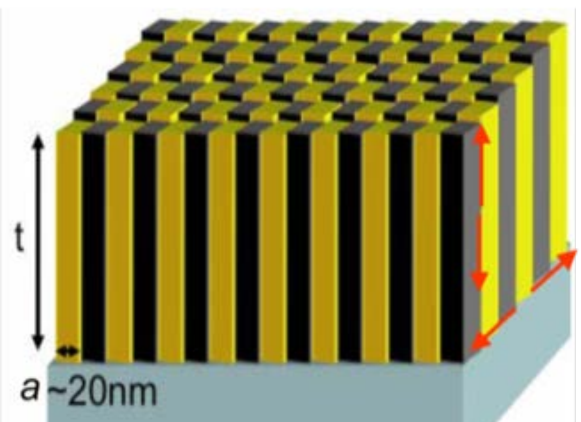
# Different Techniques Available for Growth of Thin Films

- Physical vapor deposition (**PVD**)
  - Sputtering, e-beam evaporation, molecular beam epitaxy, pulsed laser deposition
- Chemical vapor deposition (**CVD**)
  - Plasma-enhanced CVD, low pressure CVD, metal-organic CVD
- Chemical solution deposition (**CSD**)
  - Sol-gel, metal-organic decomposition (MOD)

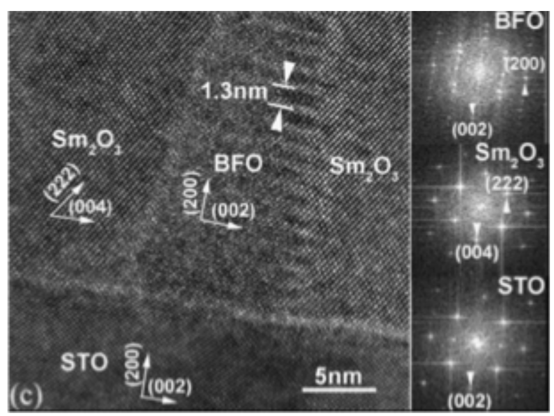
# PVD – A Powerful Technique to Synthesize Films over Multiple Length Scales



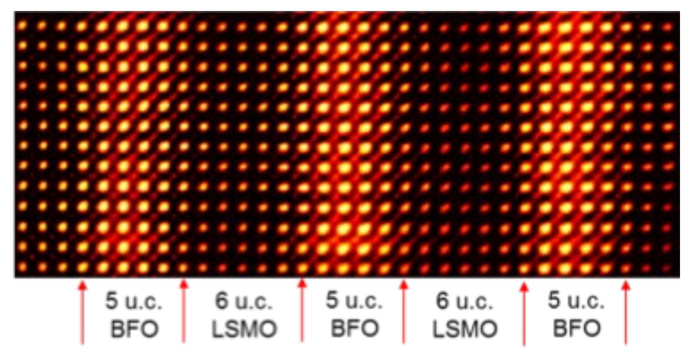



*Nat. Mater.* *7*, 314 (2008).



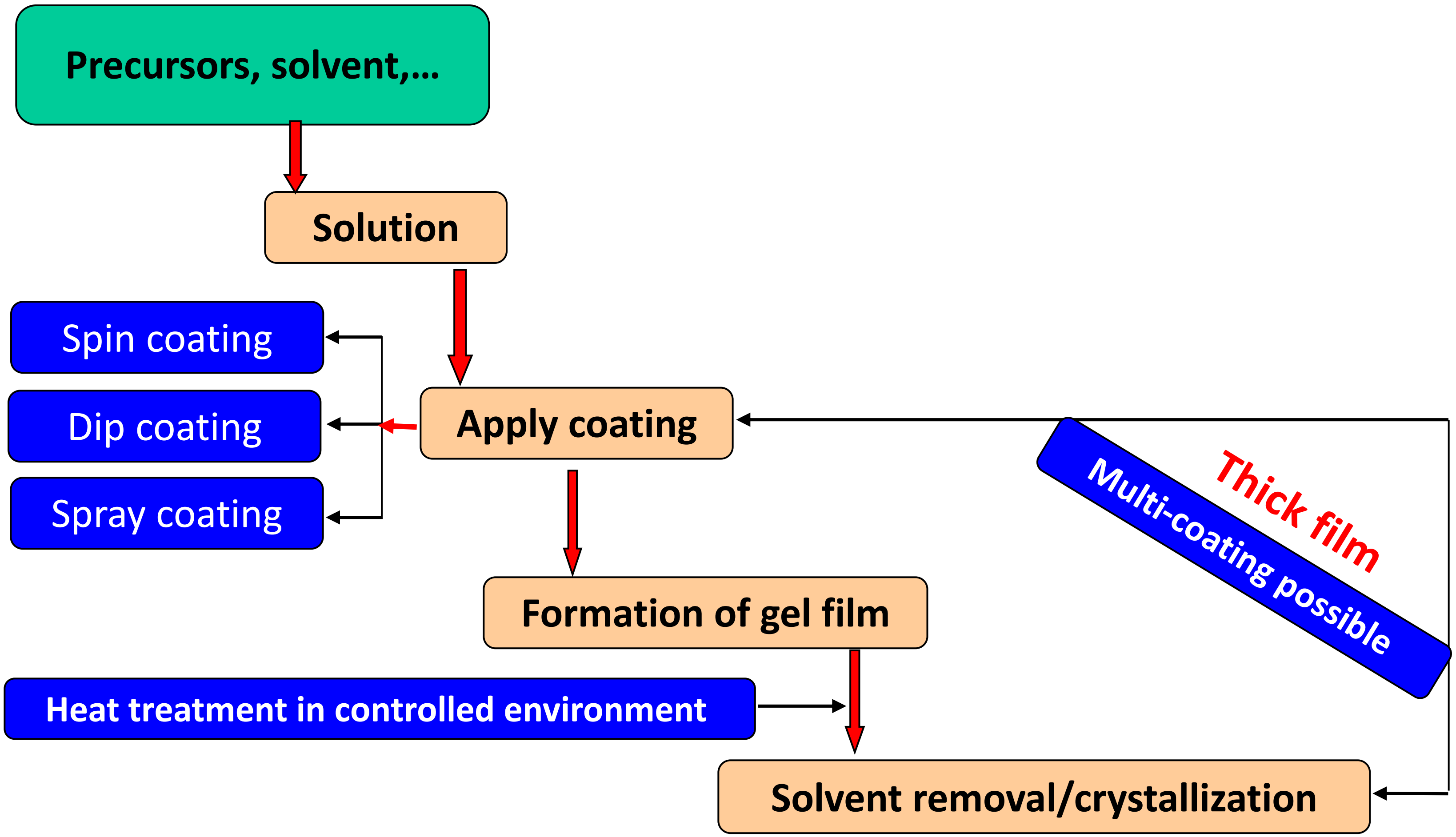

*Adv. Mater.* 21, 3794 (2009).



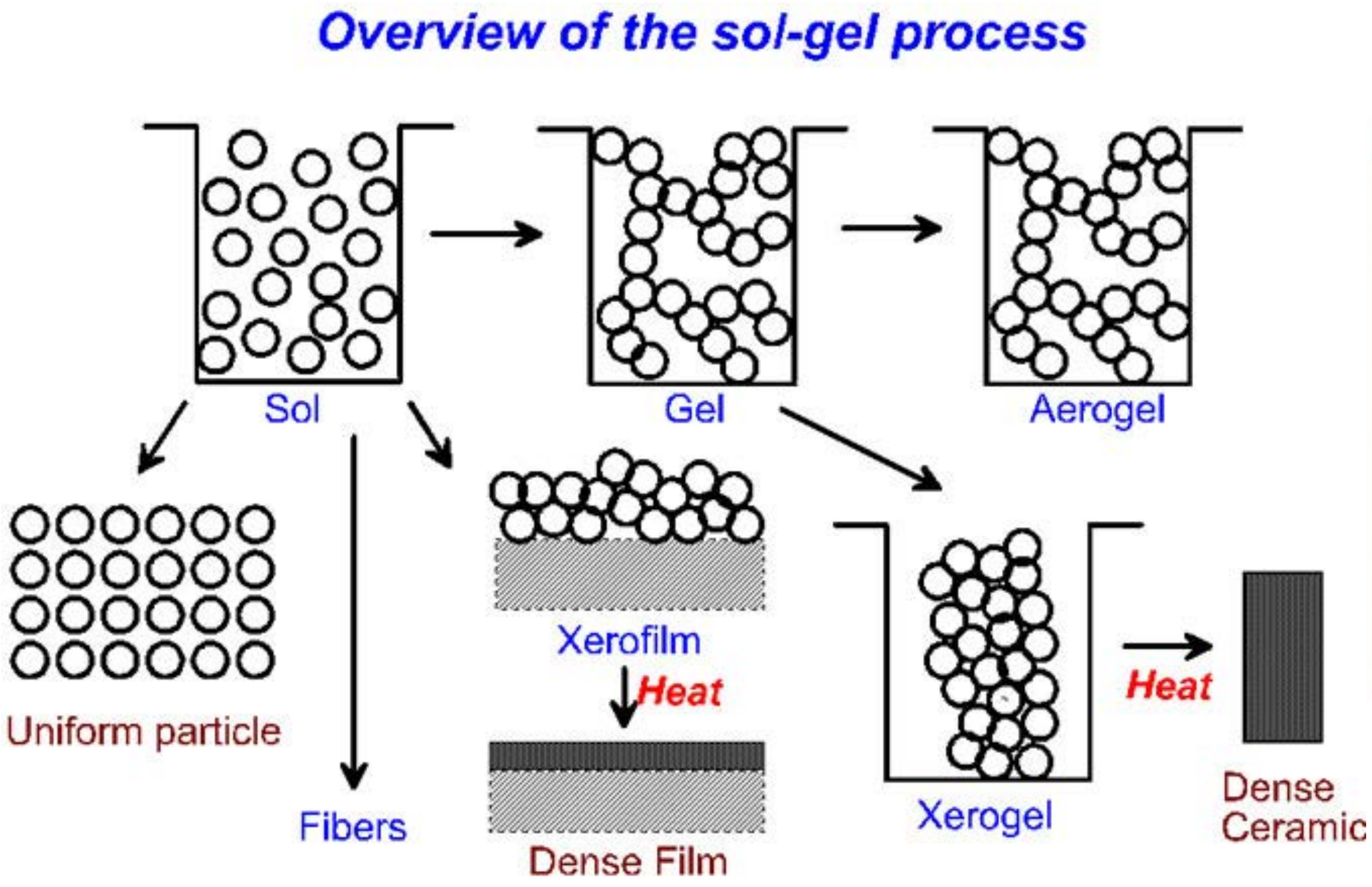
# CSD – Low Cost, Easy Setup, and Coating on Irregular Surfaces

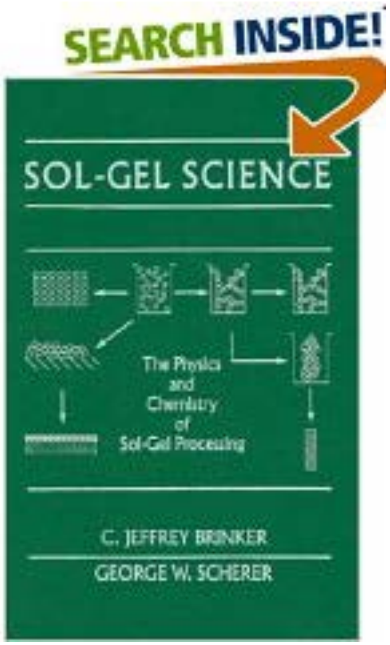
- Spin-coating
- Dip-coating
- Printing
- Painting

# Flow Chart of Typical Chemical Solution Deposition Process



# Chemical Solution Deposition: Sol-Gel Process



# Outline

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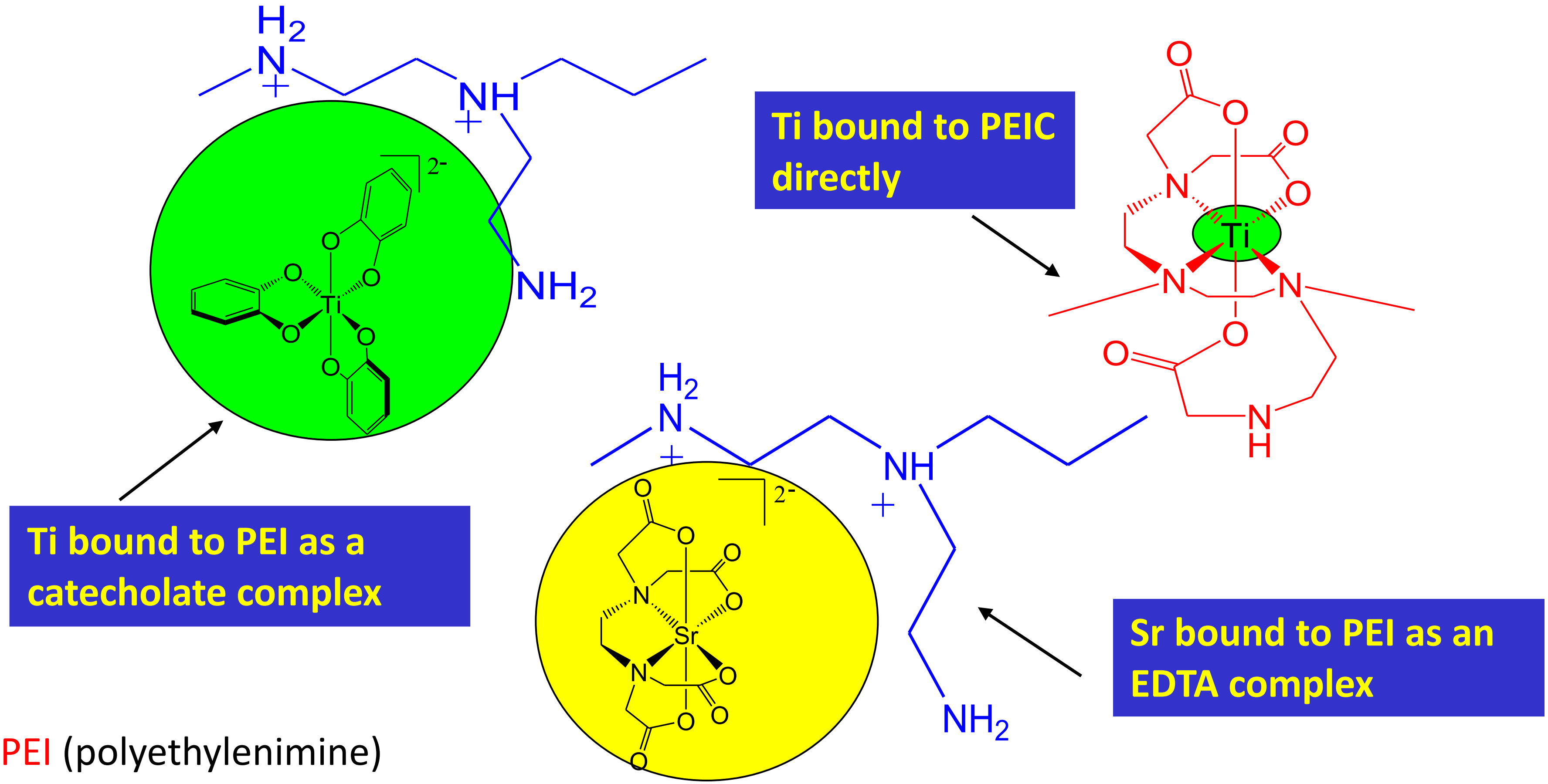
# PAD: Polymer-Assisted Deposition

- A chemical solution technique to deposit films – by mixing metal salts with water-soluble polymers
- Critical roles of polymers
  - The polymer effectively binds the metal ions
    - to stabilize the metal ions from hydrolysis in water
    - to control the solution stability, reactivity, and processibility
    - to enable filtration for the growth of high quality epitaxial complex materials
- Advantages
  - By binding metal ions to a polymer that has regular ligand sites, thin films can be deposited in a homogeneous manner.

# Schematic Illustration of Metals as Simple Salts or Complexes Bound to Polymers




PEI (polyethylenimine)
PEIC (carboxylated-polyethylenimine)
EDTA (ethylenediaminetetra-aceticacid)

# PAD Process

Select metal precursor

Water-soluble metal-salt

Mix with polymer

PEI and/or EDTA

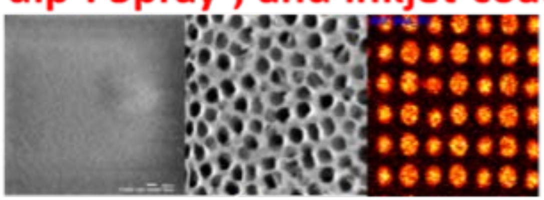
Filter solution & adjust metal concentration

Filtration to remove cations & anions not bound to polymer

Apply coating

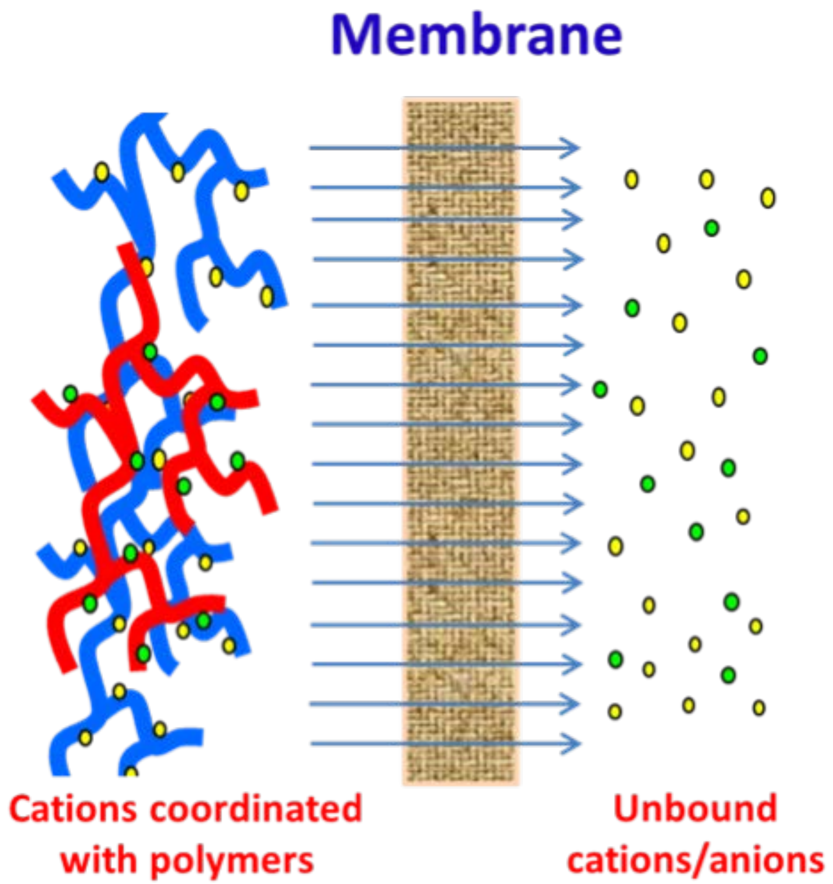
De-polymerize polymer & crystallize the film

Spin-, dip-. Spray-, and inkjet-coating

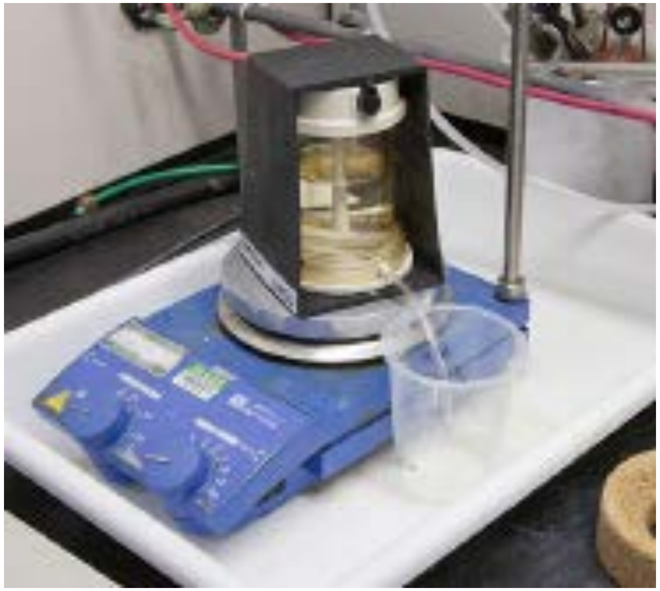


Treatment of precursor film at temperature & in controlled environment

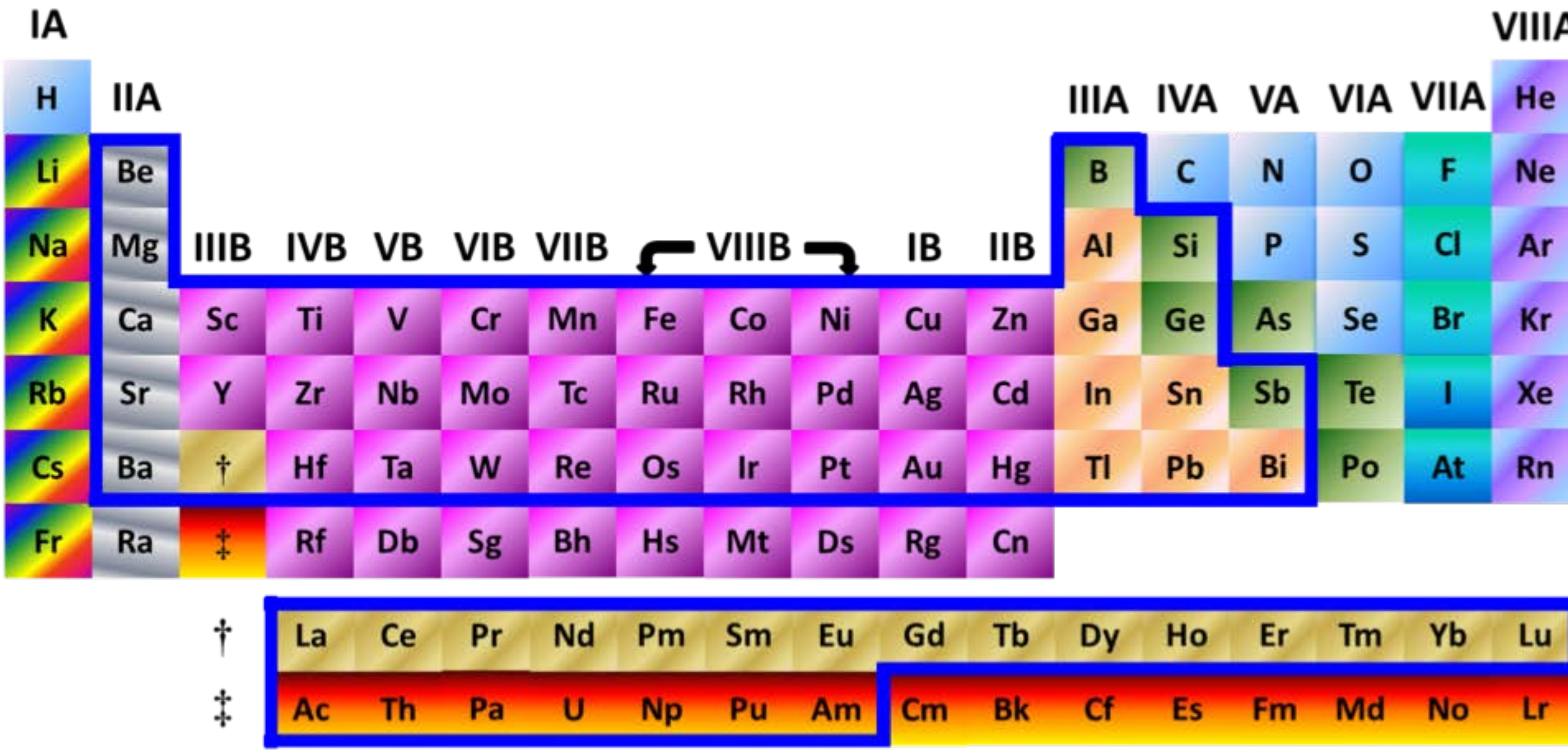
# Filtration Critical for Growth of Epitaxial Complex Films




*Chem. Soc. Rev.* 43, 2141 (2014).

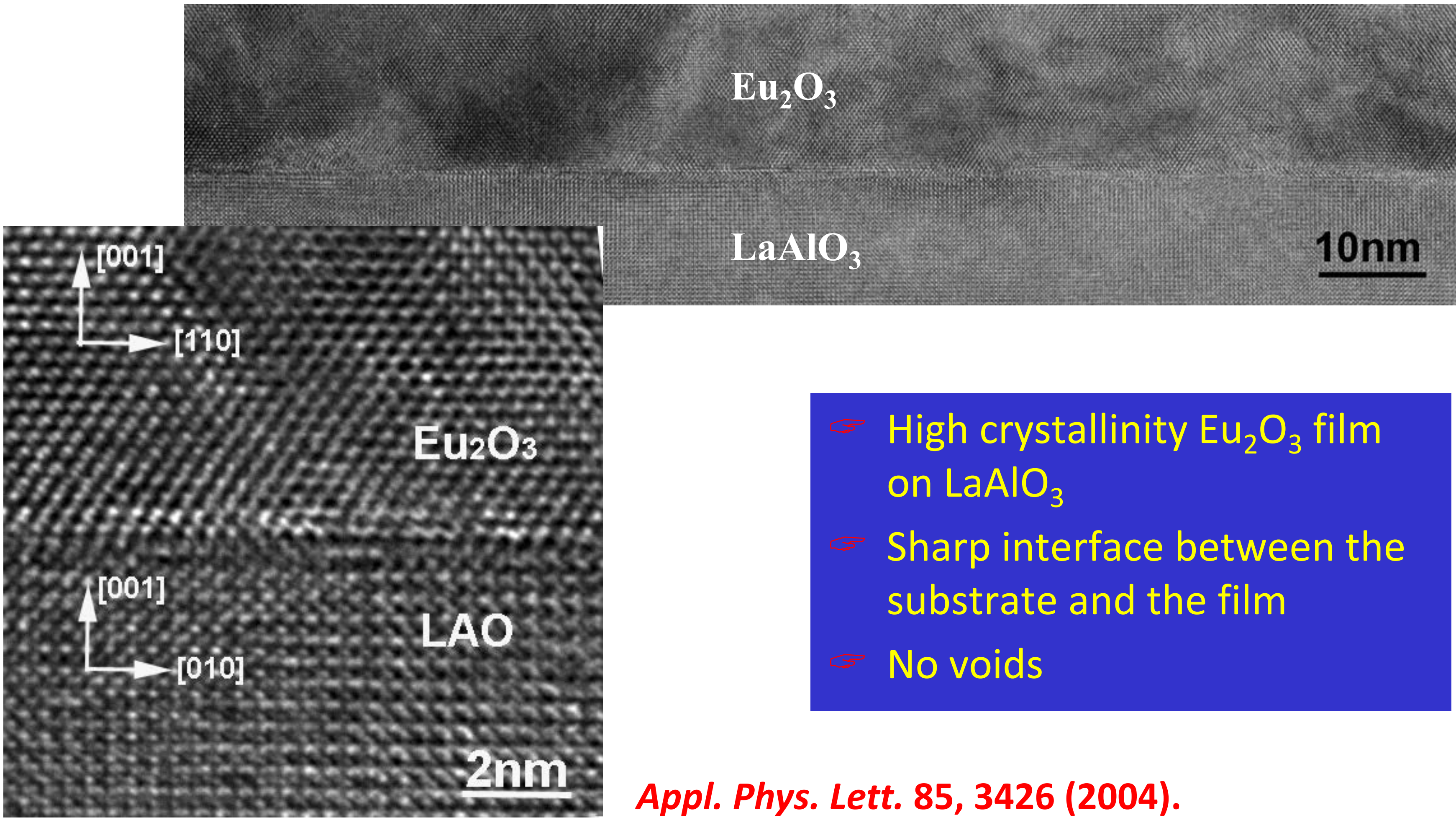


# Elements Coordinated with Polymers to Form Stable Precursor Solutions




*Chem. Soc. Rev.* 42, 439 (2013).

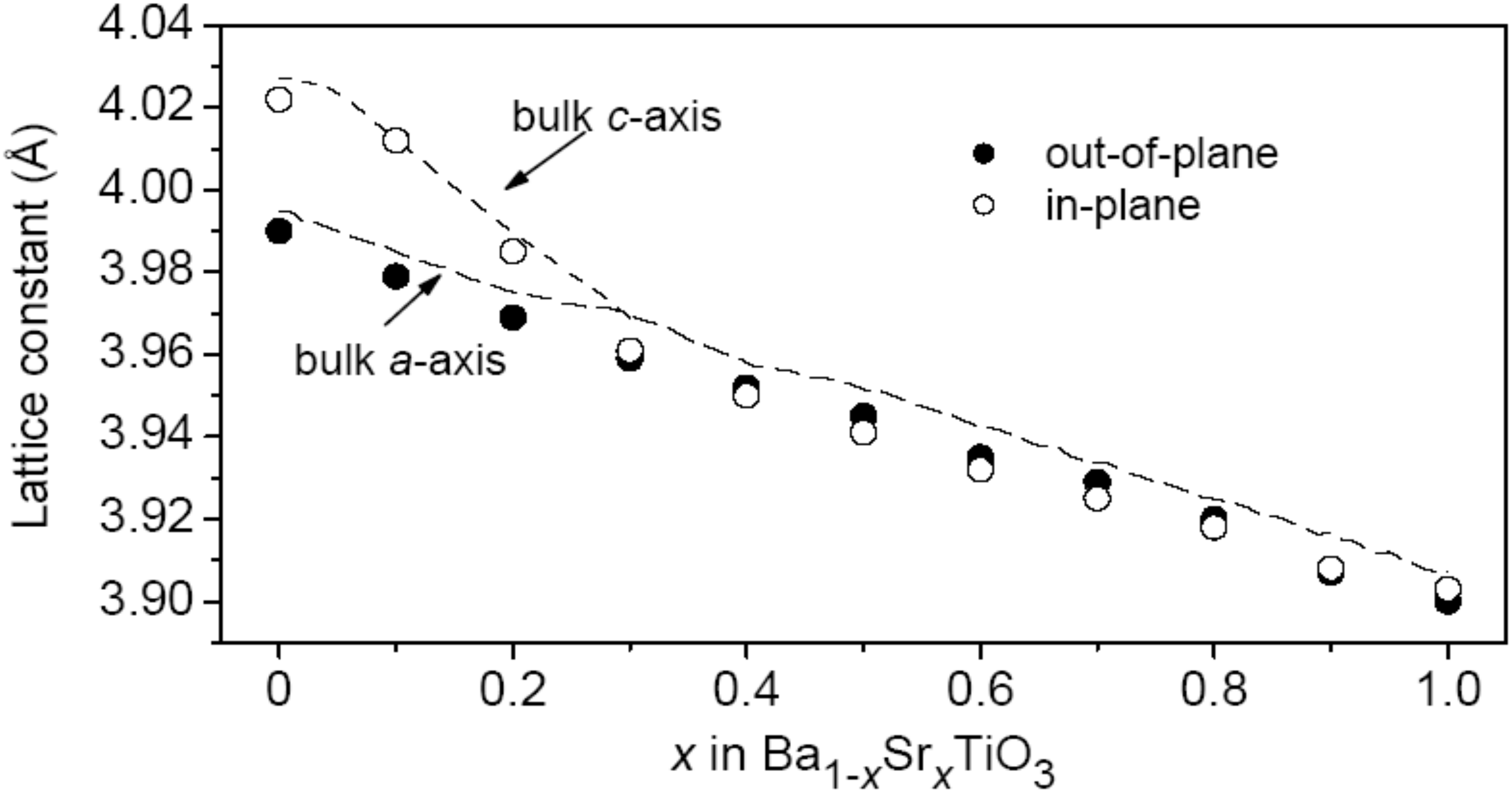
# High Quality Epitaxial Simple Metal-oxide Films as Evidenced by the Dense Film and Sharp Interface




- High crystallinity $Eu_2O_3$ film on $LaAlO_3$
- Sharp interface between the substrate and the film
- No voids

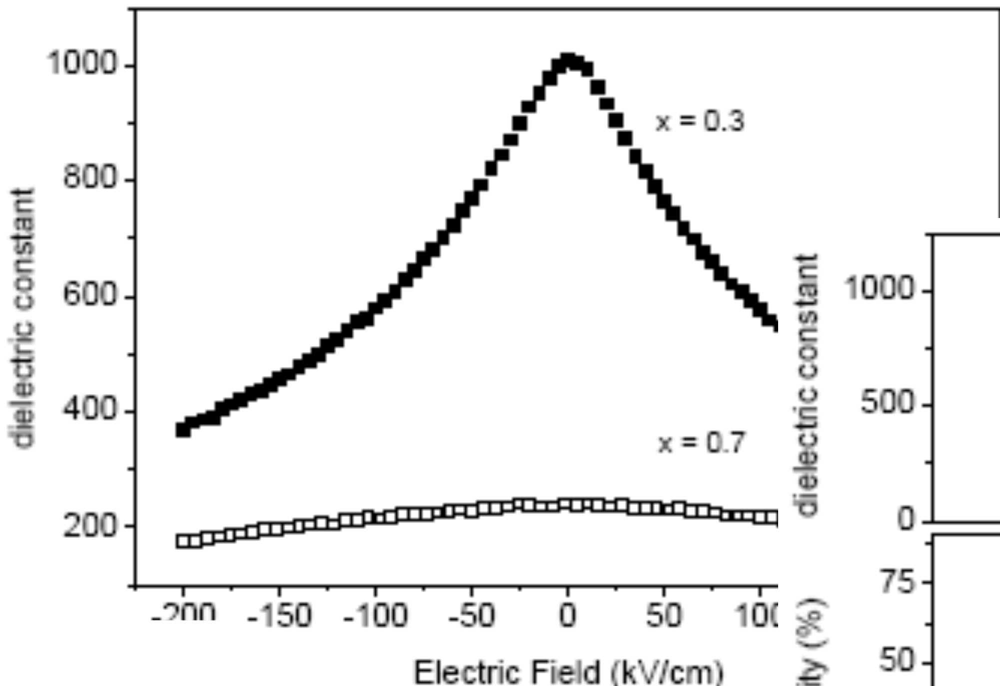
*Appl. Phys. Lett.* **85, 3426 (2004).**

# Lattice Parameters of $Ba_{1-x}Sr_xTiO_3$ as A Function of Ba/Sr Ratios

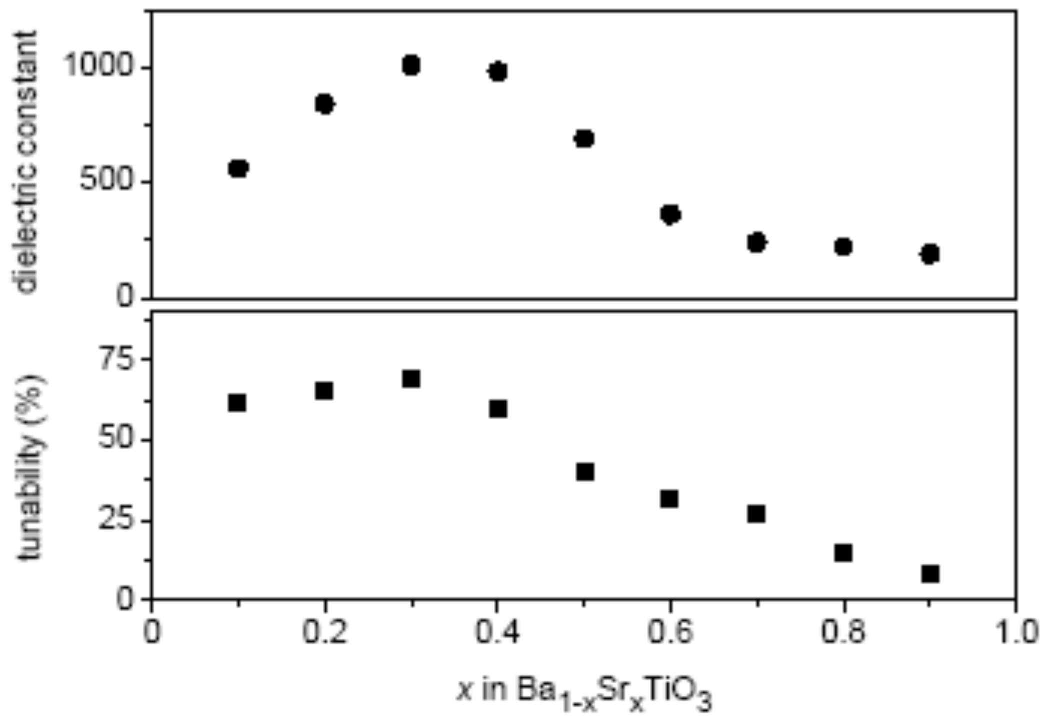



*Appl. Phys. Lett*. 85, 5007 (2004).

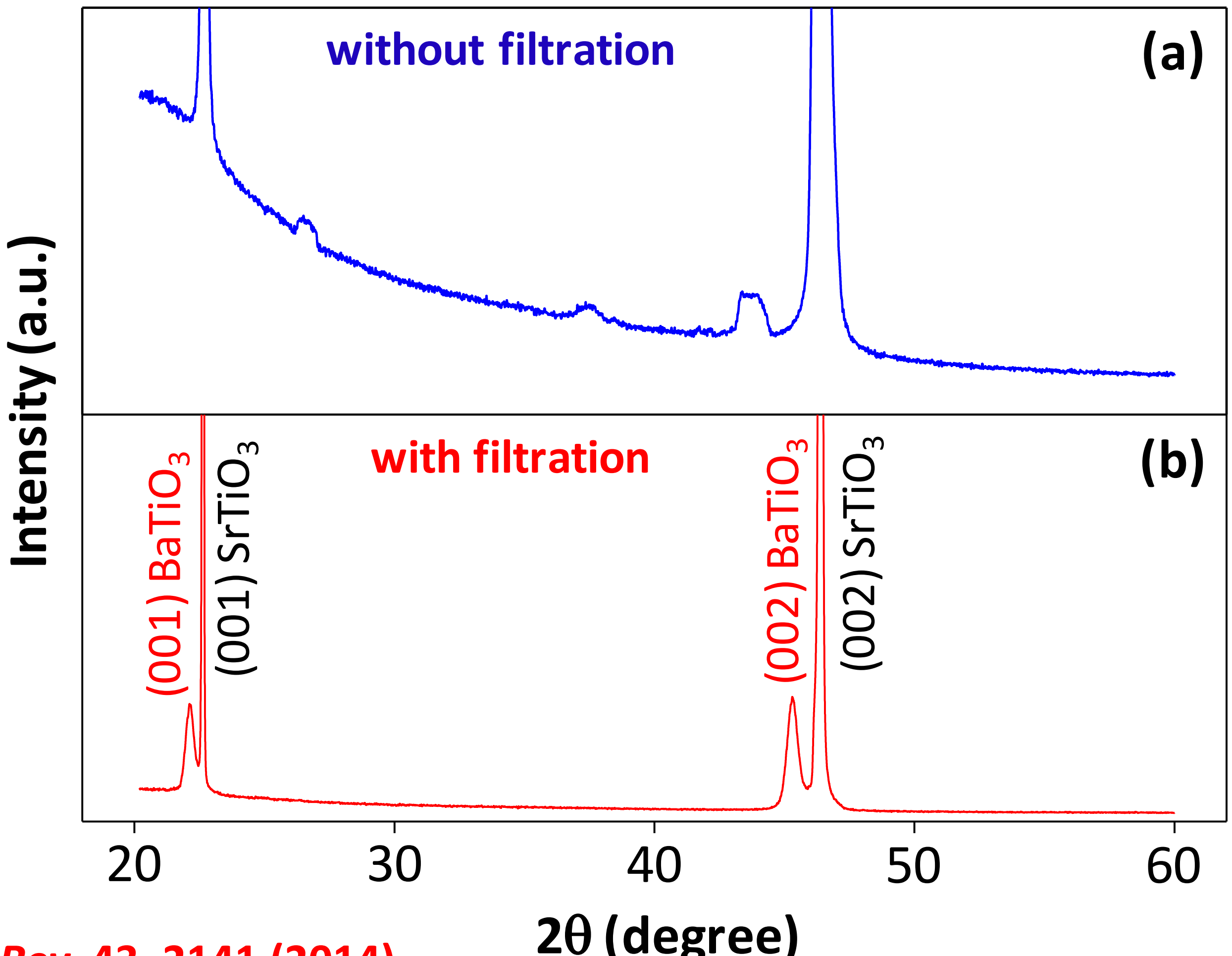
# Dielectric Properties of $Ba_{1-x}Sr_xTiO_3$ Films as A Function of Ba/Sr Ratios




**Tunability =** $T(\%) = 100 \times \dfrac{C_0 - C_V}{C_0}$



# Filtration Critical for Growth of Epitaxial Complex Metal Oxide Films




*Chem. Soc. Rev.* **43, 2141 (2014).**

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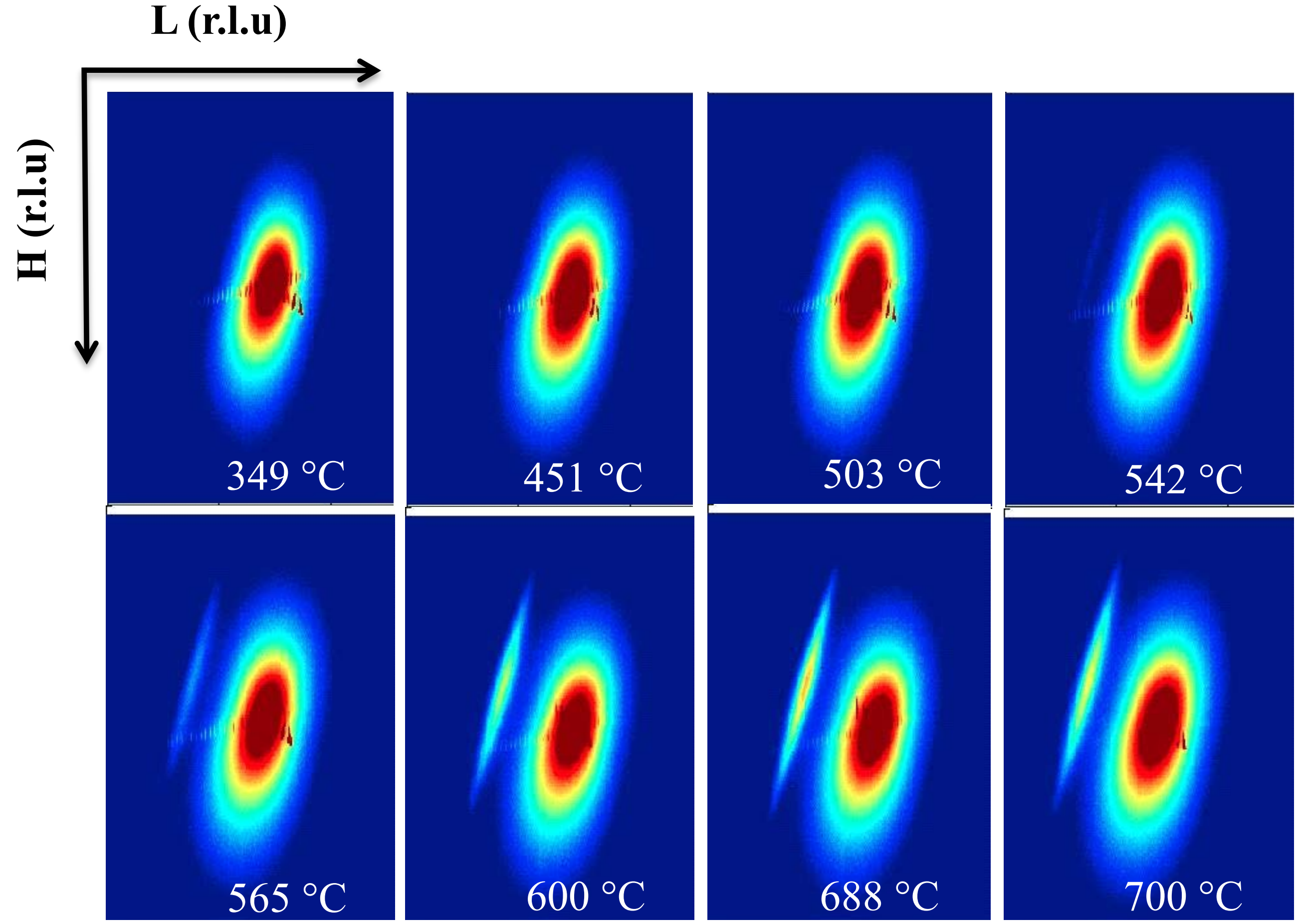
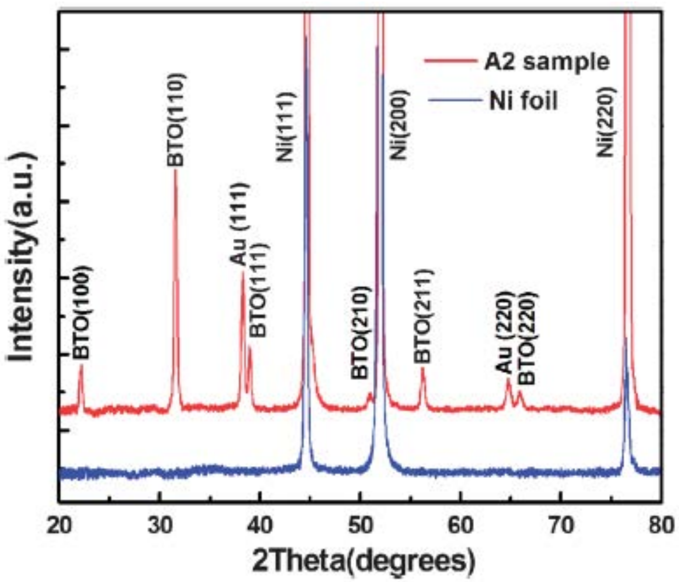
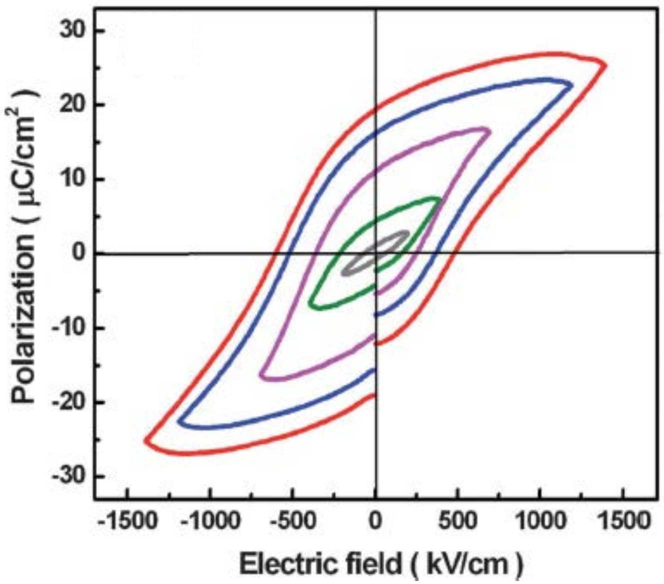



*Chem. Soc. Rev.* 43, 2141 (2014).

# $BaTiO_3$ Films Deposited on Polycrystalline Ni Substrates




Ni: 0.5 mm
BTO: 500 nm

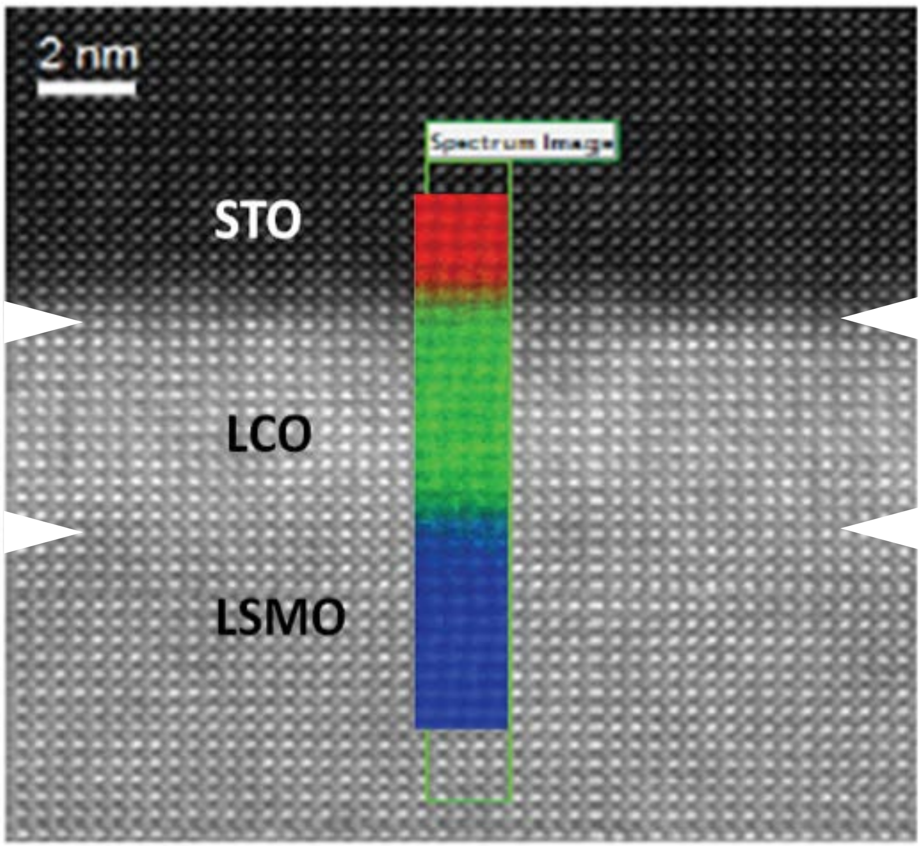


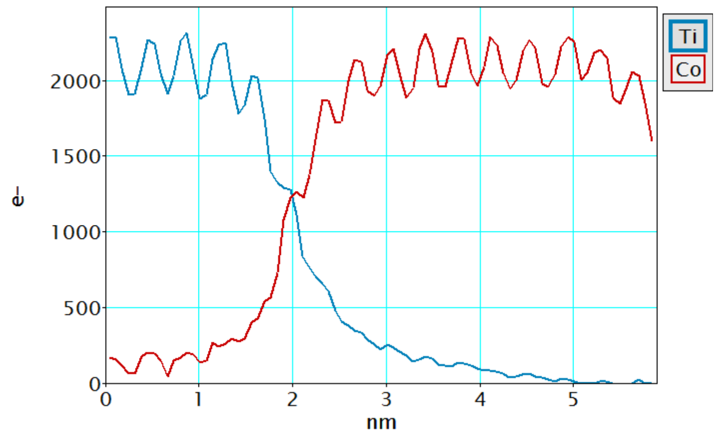

**Typical XRD θ–2θ patterns of as-grown $BaTiO_3$ film on polycrystalline Ni**

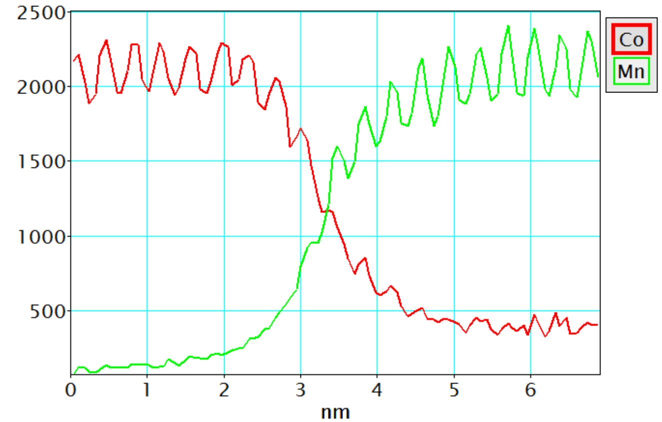
**Polarization of a $BaTiO_3$ film as a function of the electric field at room temperature**

*J. Mater. Chem. C* **2**, 708 (2014).

# Epitaxial Growth of $La_{0.7}Sr_{0.3}MnO_3/LaCoO_3$ on $SrTiO_3$ by PAD

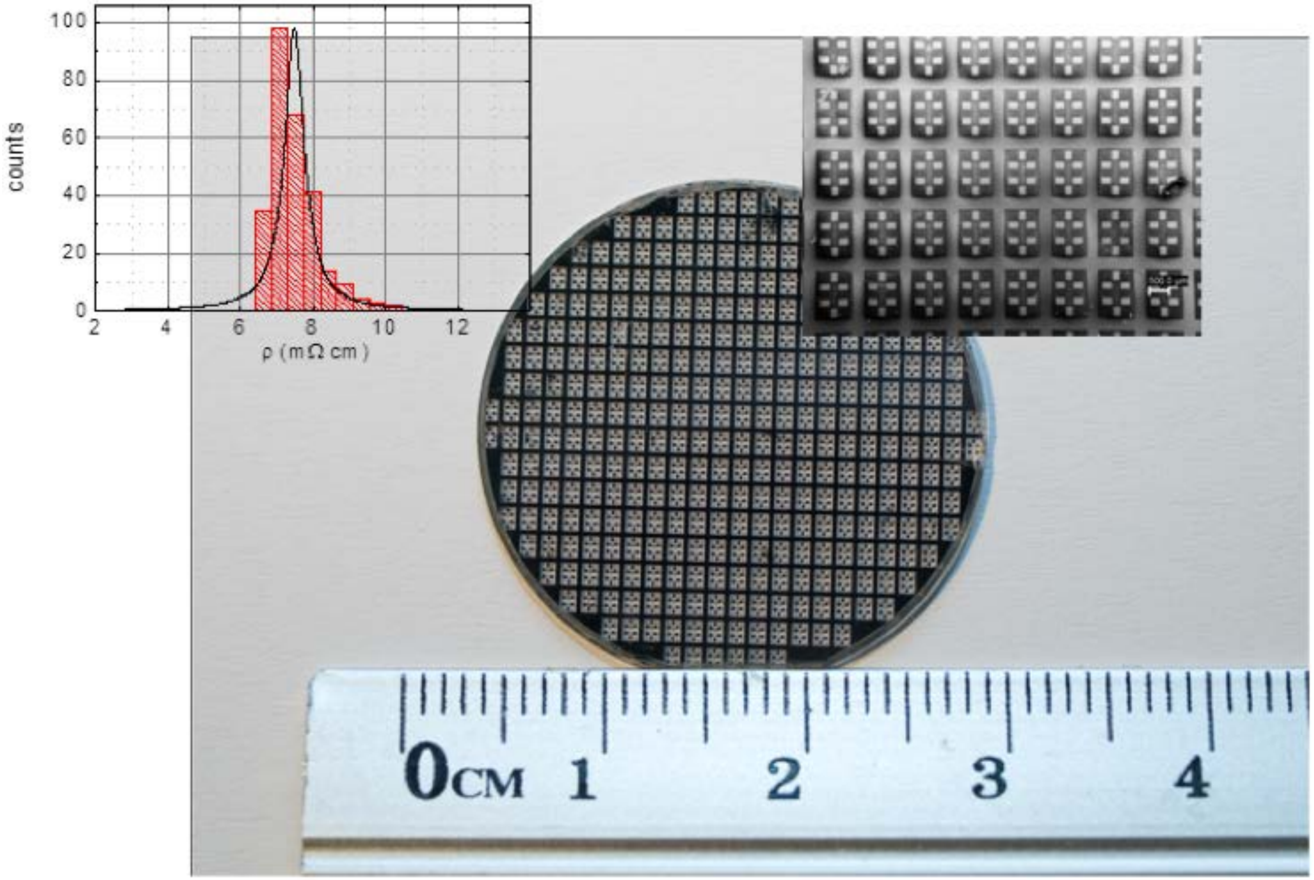



By F. Rivadulla, Universidad de Santiago de Compostela, Spain

# Uniform Deposition of Epitaxial Complex Metal Oxide Films by PAD




$La_{0.7}Sr_{0.3}MnO_3$
18 nm

By F. Rivadulla, Universidad de Santiago de Compostela, Spain

# Polymer-assisted deposition of metal-oxide films

Q. X. JIA[1]*, T. M. MCCLESKEY[2], A. K. BURRELL[2], Y. LIN[1], G. E. COLLIS[2], H. WANG[1], A. D. Q. LI[3] AND S. R. FOLTYN[1]
[1]Superconductivity Technology Center, Division of Materials Science and Technology, and [2]Structural and Inorganic Chemistry, Division of Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
[3]Deptartment of Chemistry, Washington State University, Pullman, Washington 99164, USA
*e-mail: qxjia@lanl.gov

Appl. Phys. Lett. 99, 083113 (2011); doi:10.1063/1.3629993 (*3 pages*)

## Magnetoresistance in epitaxial thin films of $La_{0.85}Ag_{0.15}MnO_3$ produced by polymer assisted deposition

R. Cobas[1], S. Muñoz-Perez[1], J. M. Cadogan[1], T. Puig[2], and X. Obradors[2]
[1]*Department of Physics and Astronomy, University of Manitoba, Winnipeg, R3T 2N2 Manitoba, Canada*
[2]*Institut de Ciència dels Materials de Barcelona, CSIC, Campus de la UAB, 08193 Bellaterra, Spain*

*Nature Protocols* **5**, 1440 - 1446 (2010)
Published online: 22 July 2010 | doi:10.1038/nprot.2010.105

**Subject Category:** Chemical modification

## Polymer-assisted deposition of homogeneous metal oxide films to produce nuclear targets

Mazhar N Ali[1,2], Mitch A Garcia[1,2], T Parsons-Moss[1,2] & Heino Nitsche[1,2]

# Outline

- Introduction
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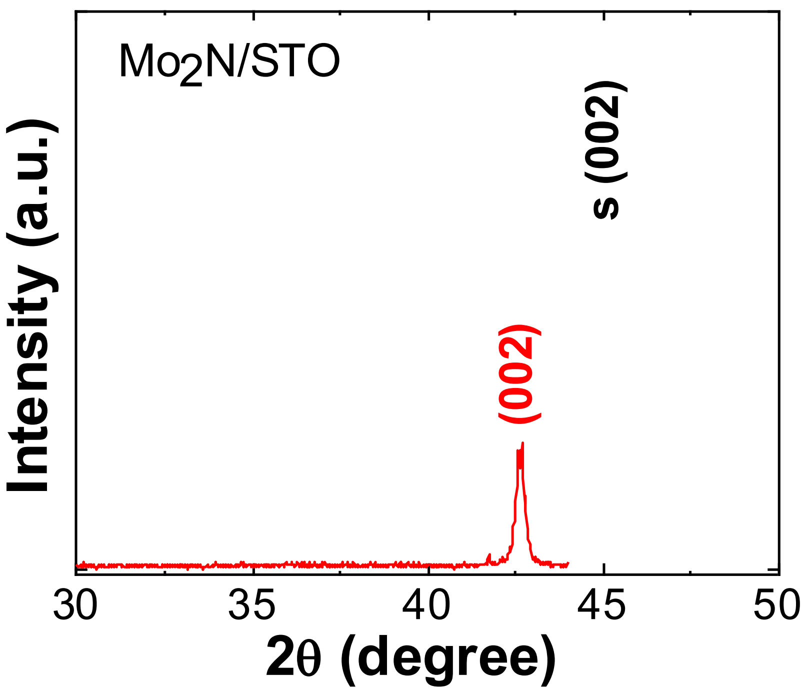
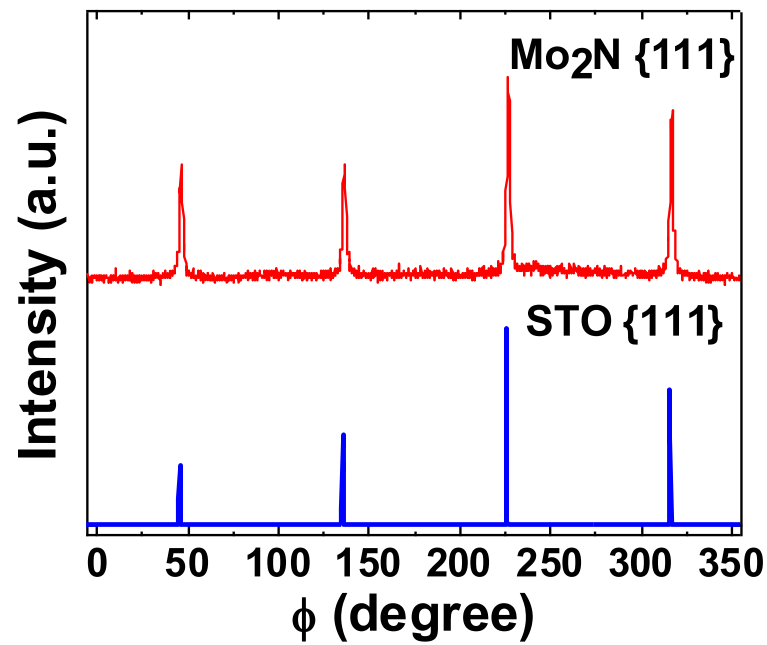
# Epitaxial $Mo_2N$ Films on $SrTiO_3$



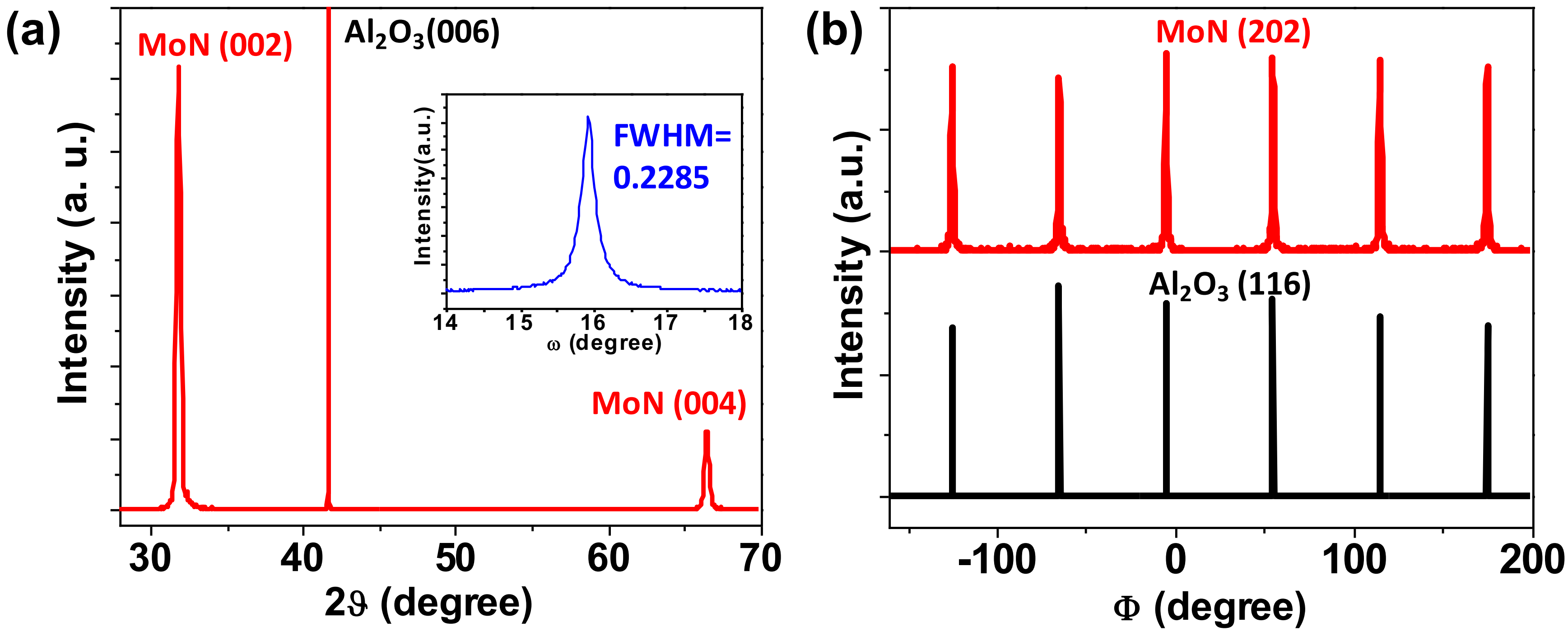




$\gamma$ - $Mo_2N$ (cubic)

$a$ = 0.416 nm

*J. Phys. Chem. C* 115, 17880 (2011*).*

# Epitaxial MoN Films on c-cut Sapphire

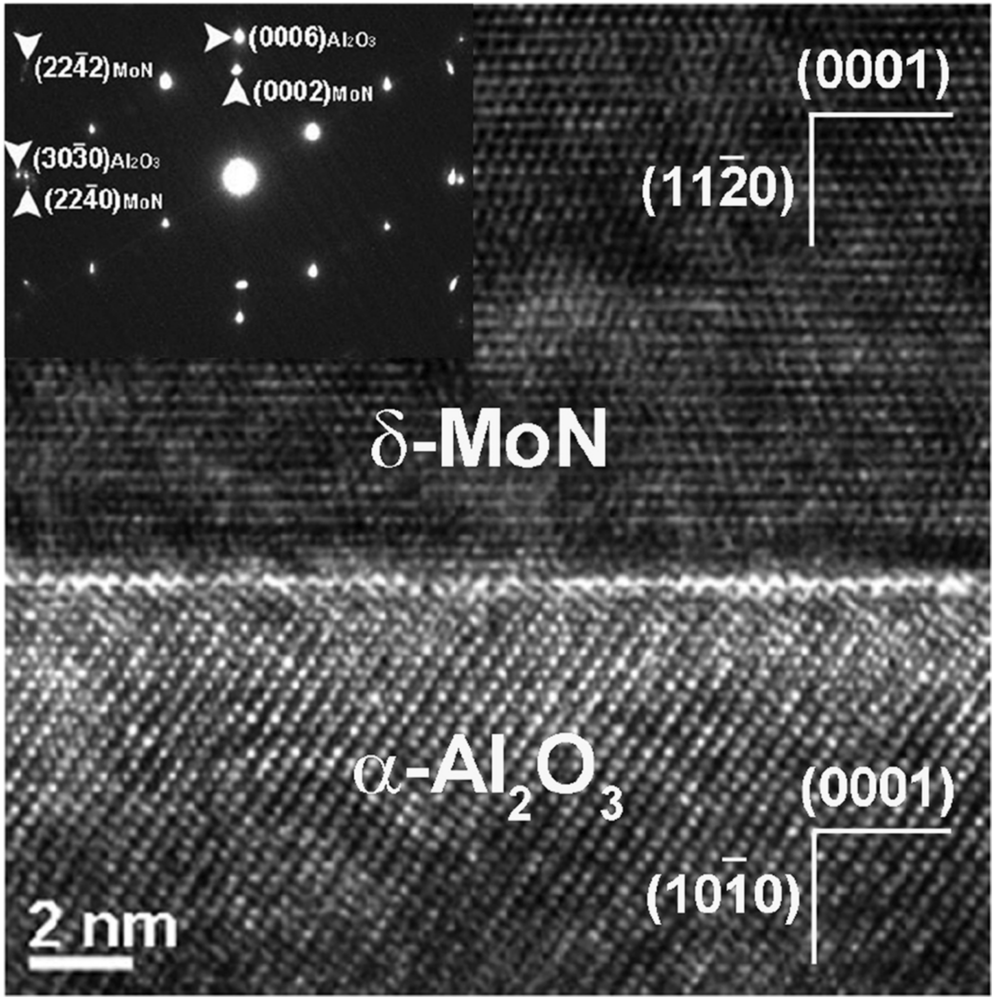



δ-MoN (hexagonal)

*a* = 0.572 nm

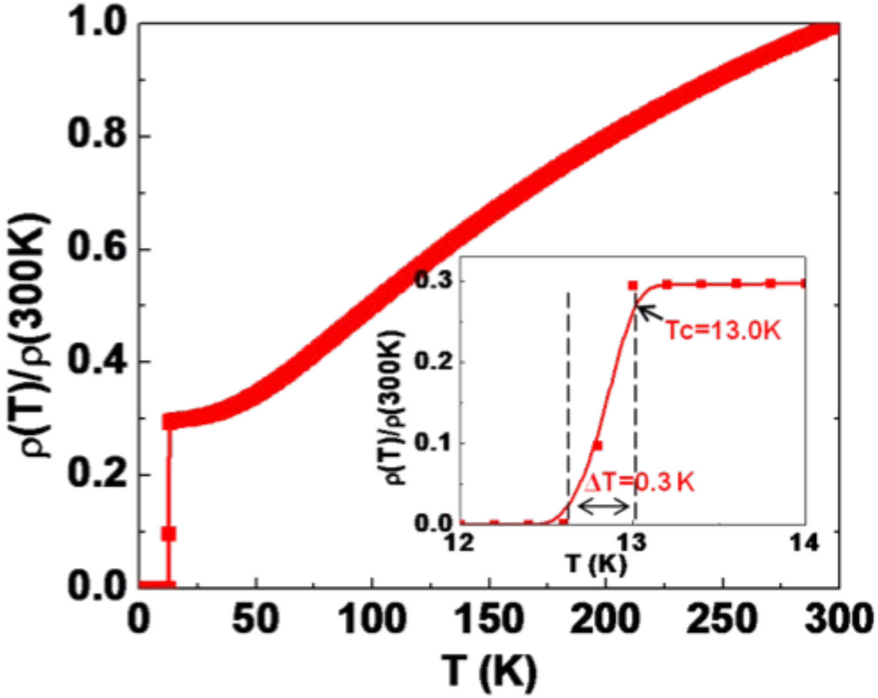
*c* = 0.562 nm

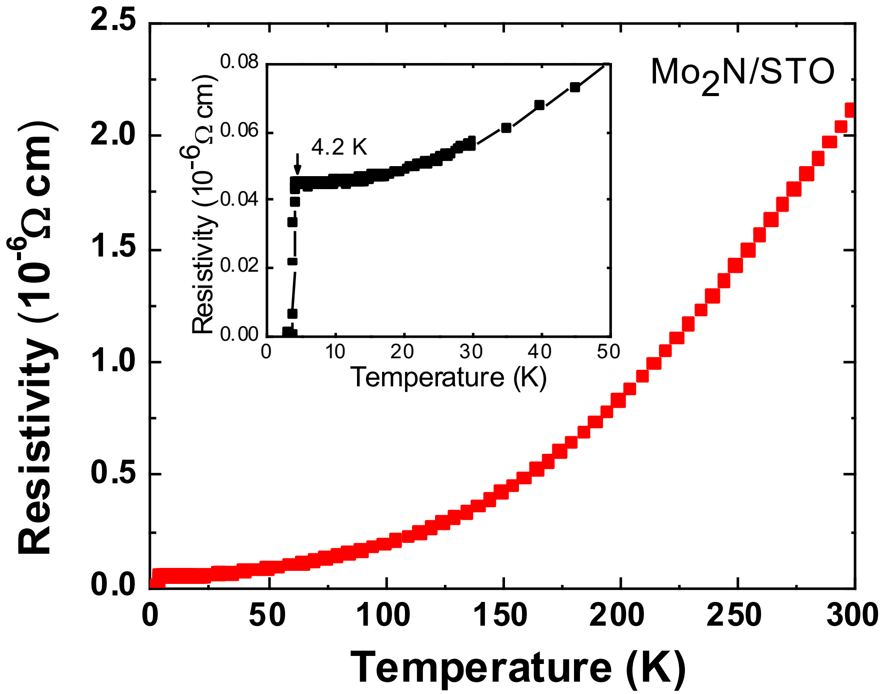
# Sharp Interface between the Substrate and the MoN Film



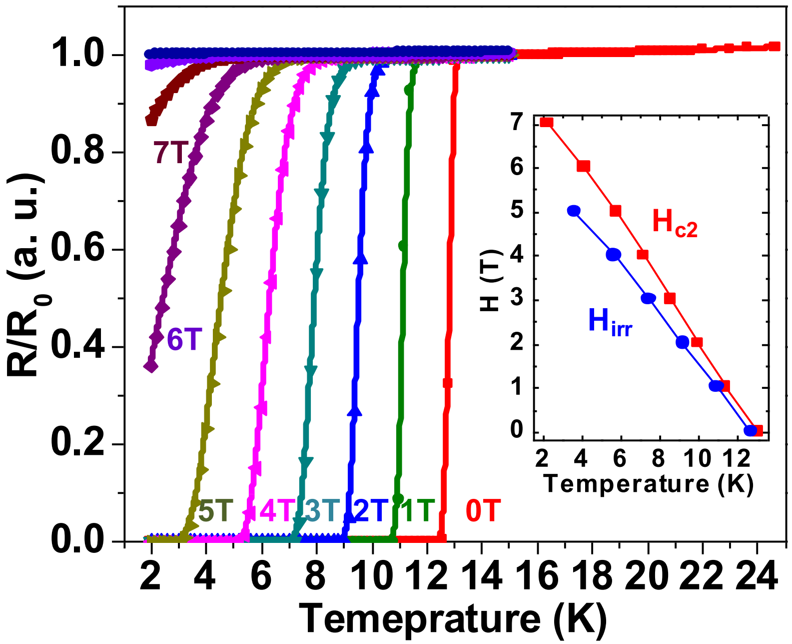

*J. Am. Chem. Soc.* **133, 20735 (2011).**

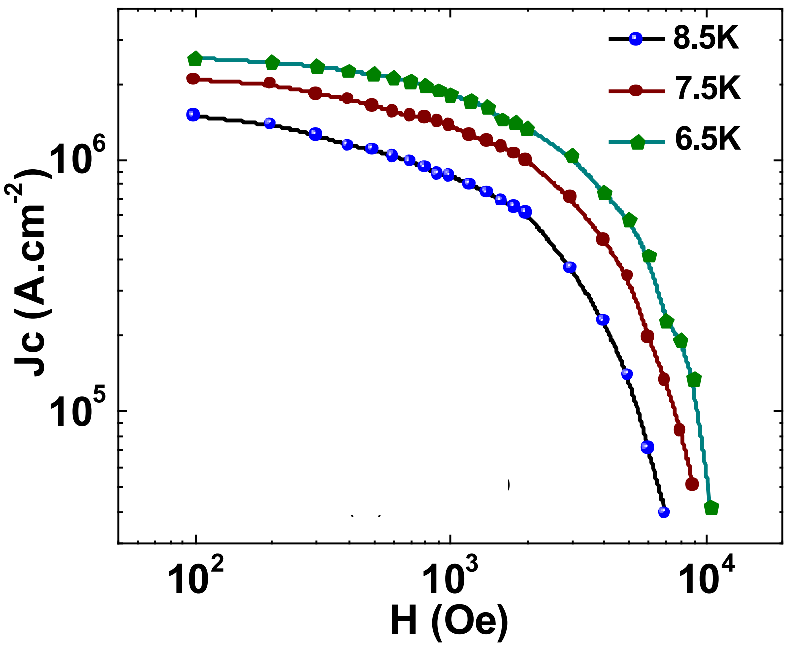
# MoN and $Mo_2N$ Films with Different Superconducting Properties as Expected



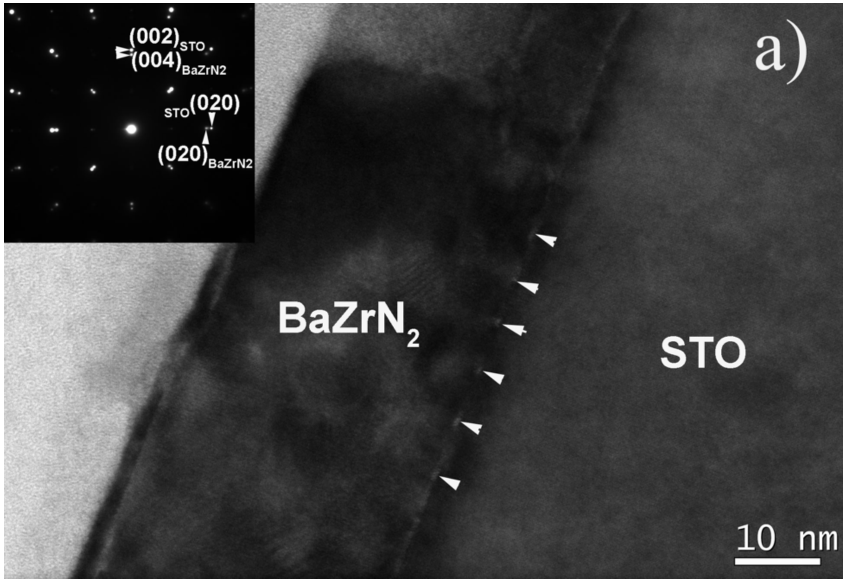



# Superconducting Properties of the MoN Films

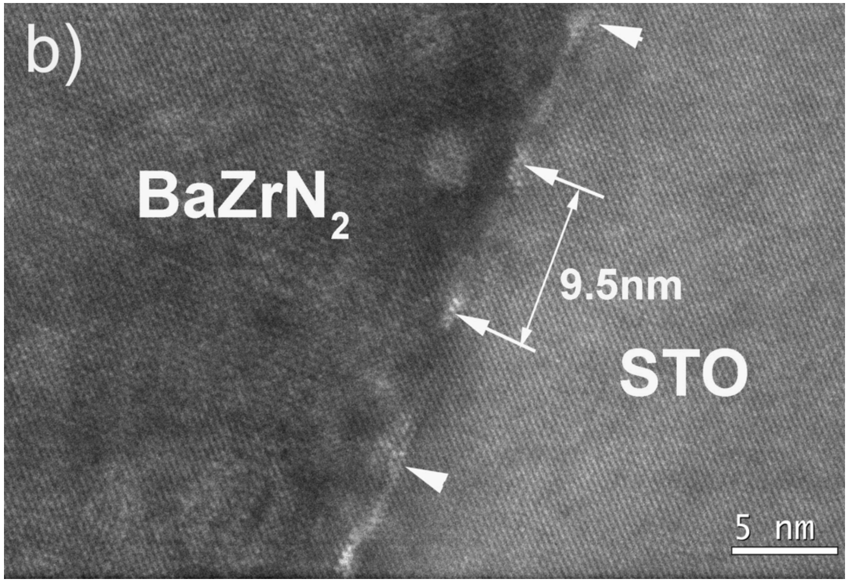


# Well Controlled Interface between the Epitaxial $BaZrN_2$ Film and the Substrate




*$BaZrN_2$: $a$* = 4.08 Å
$SrTiO_3$: $a$ = 3.901 Å



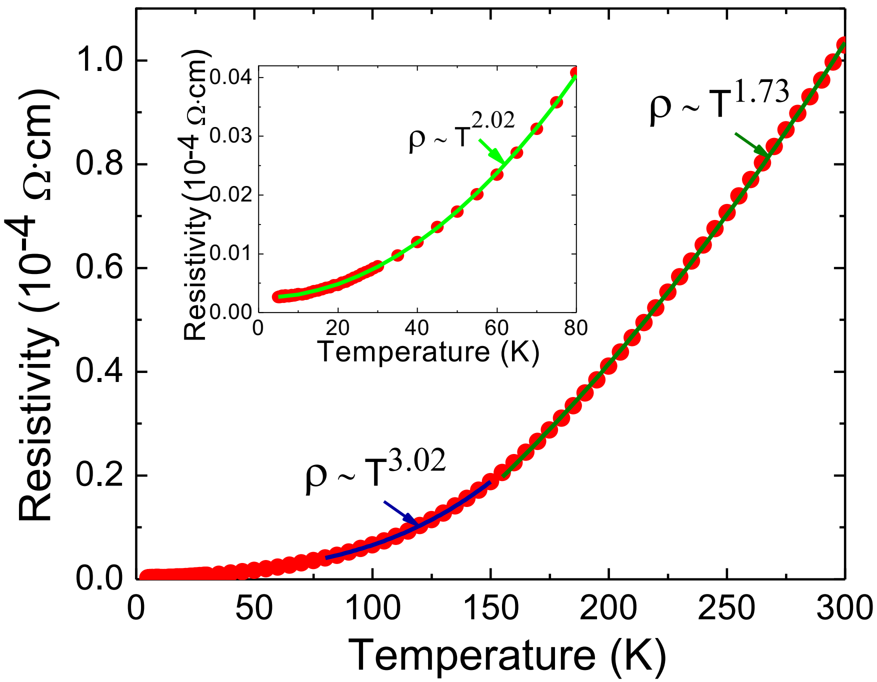

The lattice misfit: 4.25 %

Dislocation spacing ~ 9.5nm

23 $a_{BZN}$ to 24 $a_{STO}$

***Angew. Chemie. Int. Ed.* 121, 1518 (2009).**

# Very Large Residual Resistivity Ratio of High Quality $BaZrN_2$ Films




$\rho(T) = \rho_0 + AT^m$

Different conduction mechanisms

- electron-electron scattering (5-80 K)
- electron-phonon scattering (80-155 K)
- disordered localized magnetic moment (160-300 K)

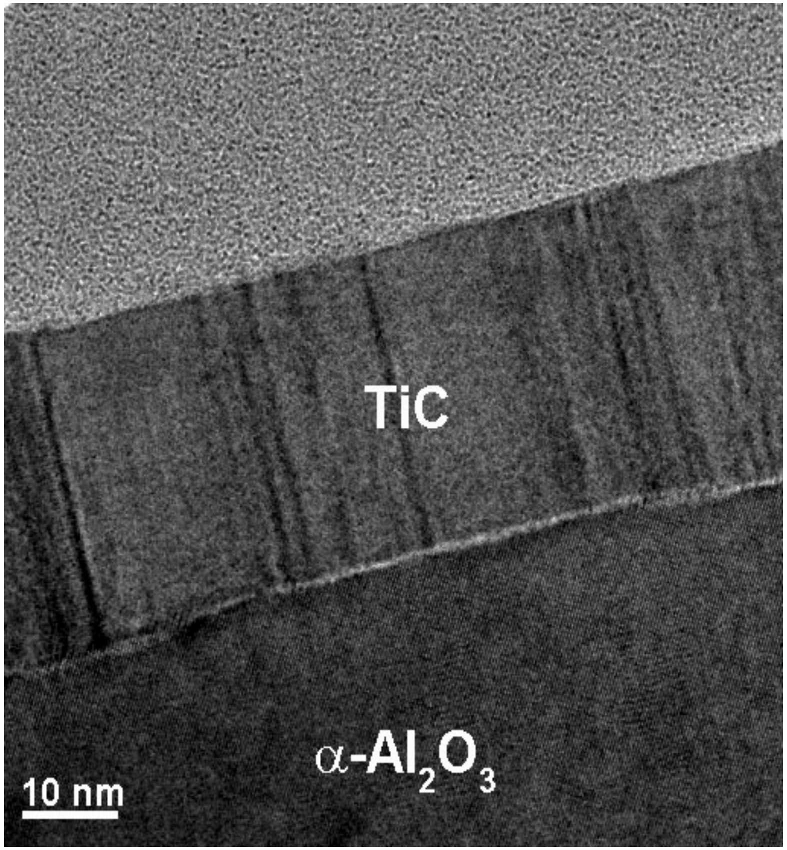
Residual resistivity ratio

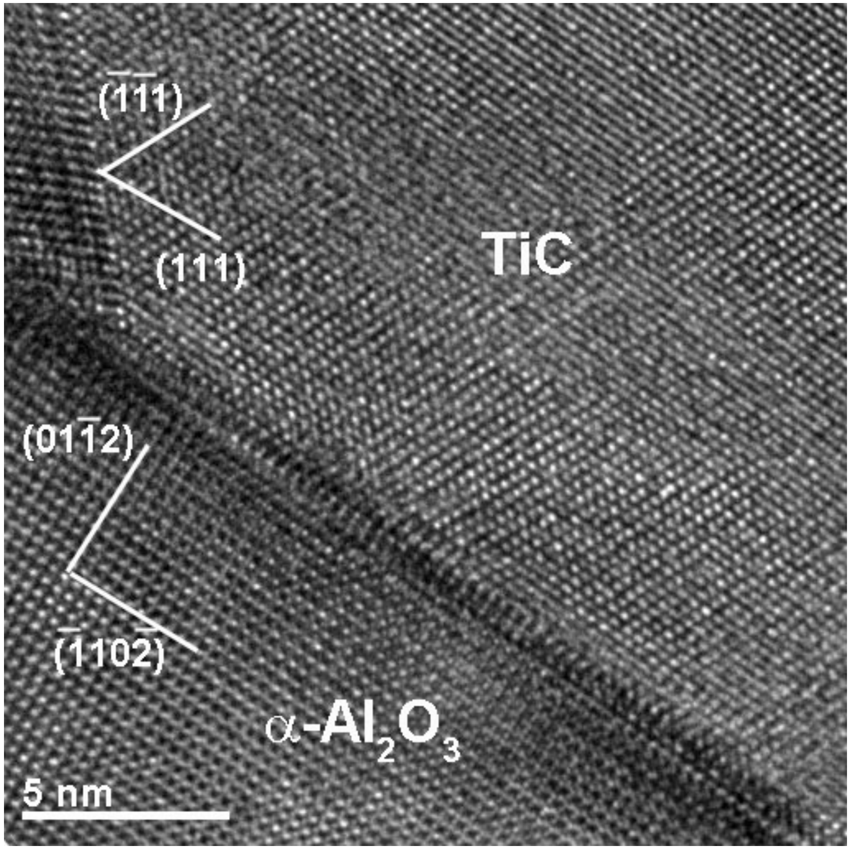
$RRR = \rho_{300K}/\rho_{5K} = 396$

# Outline

- Introduction
- Experimental details and results
  - Metal-oxide films
  - Metal-nitride films
  - Metal-carbide films
  - Other coatings
- Summary

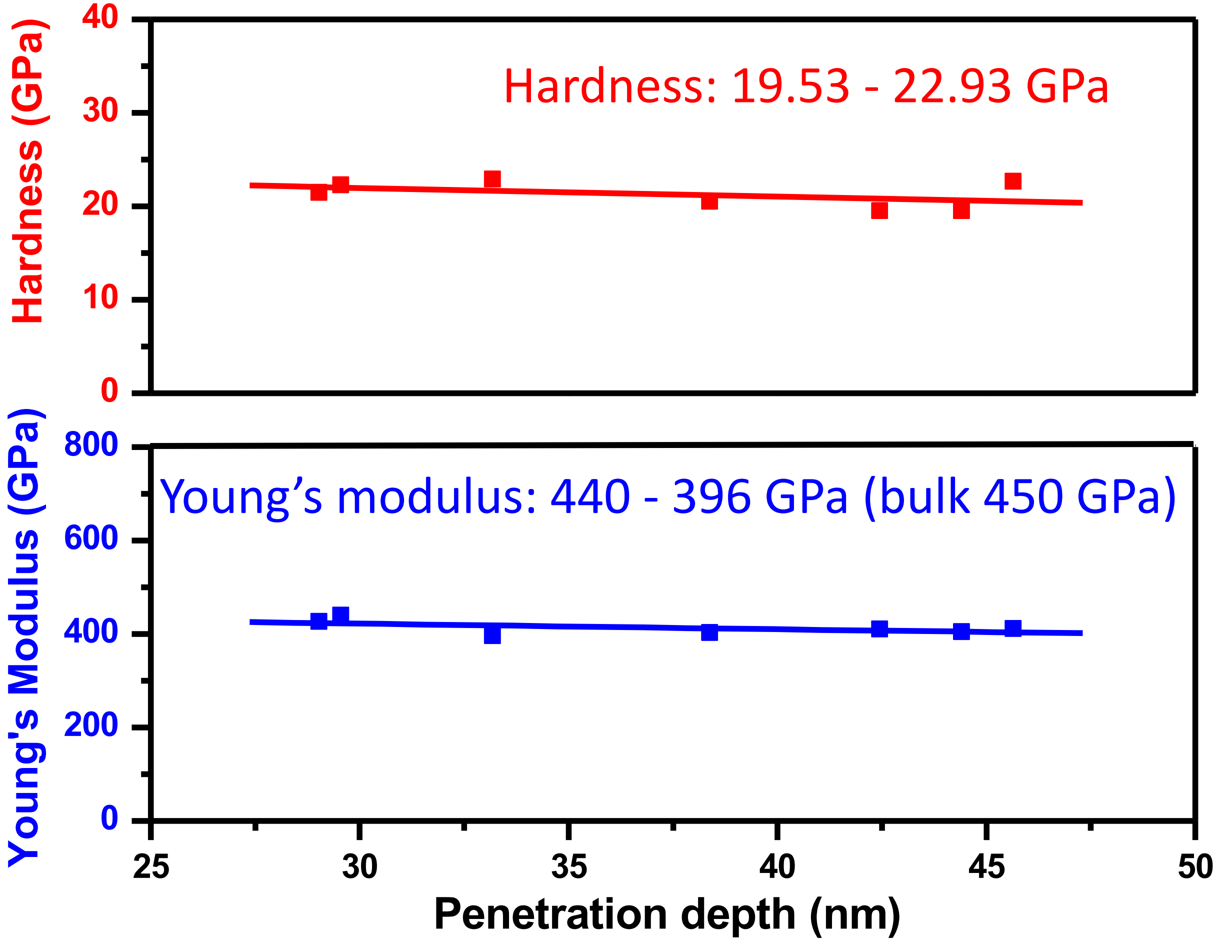
# Heteroepitaxial Simple Metal-Carbide Film by PAD



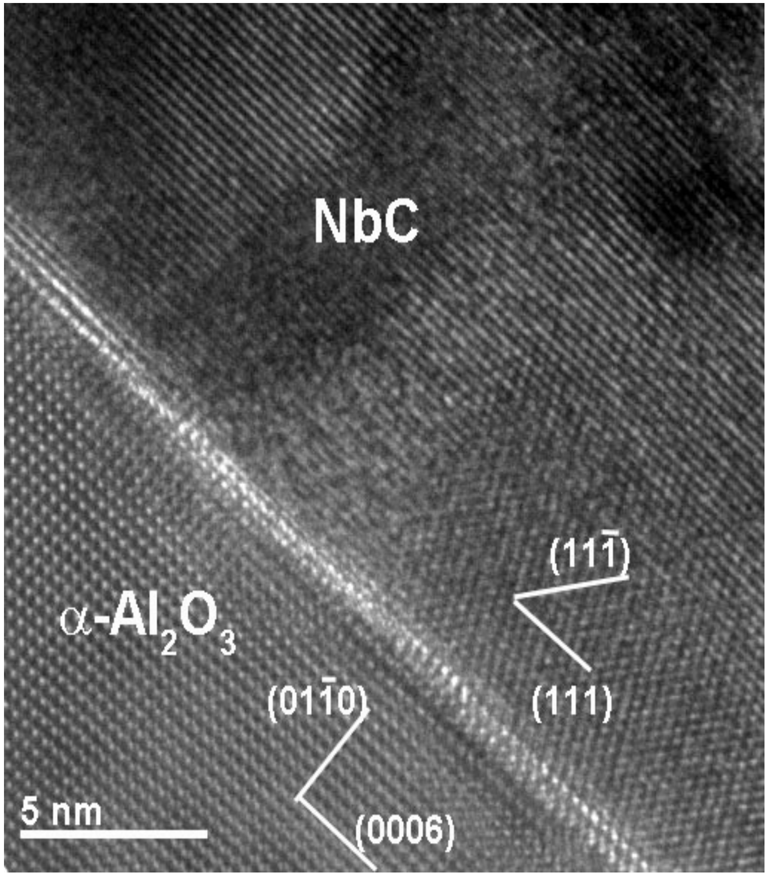



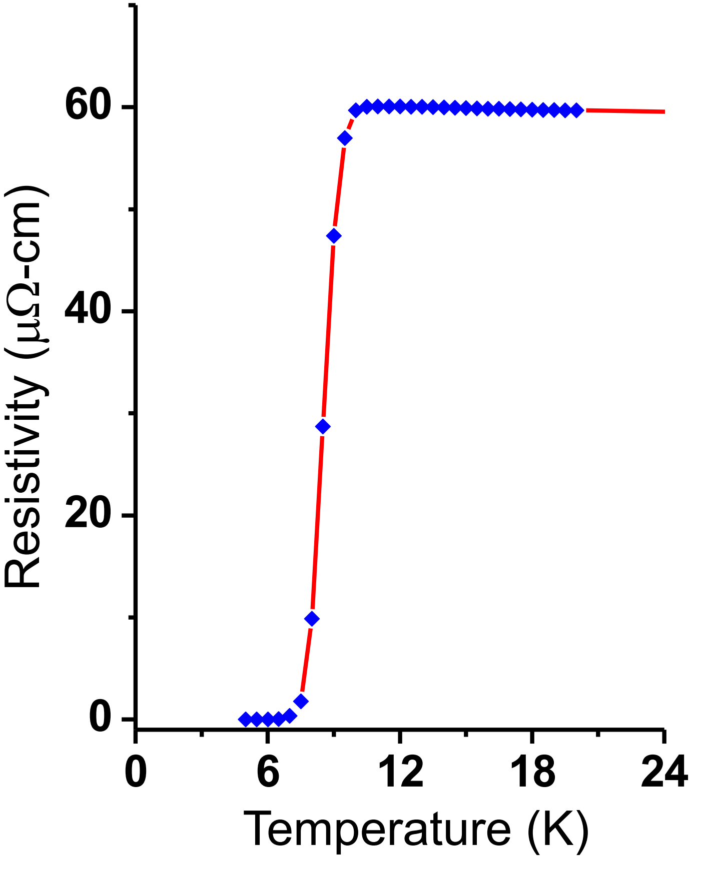

*J. Am. Chem. Soc. 132, 2516* (2010).

# Desired Mechanical Properties of TiC Films



# High Quality NbC Film with a Superconducting Transition Temperature of 10 K




*Chem. Commun.* 46, 7837 (2010).

# Outline

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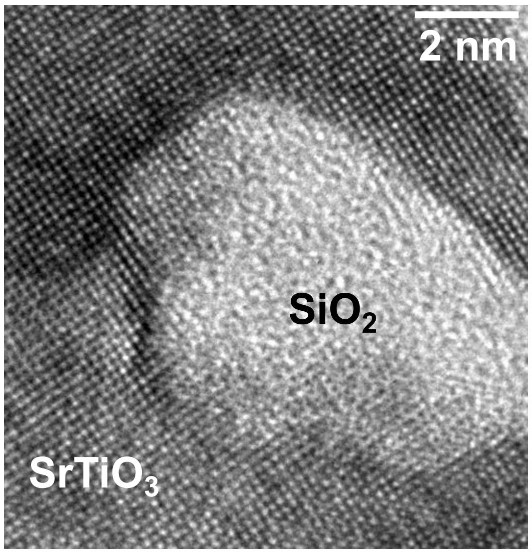
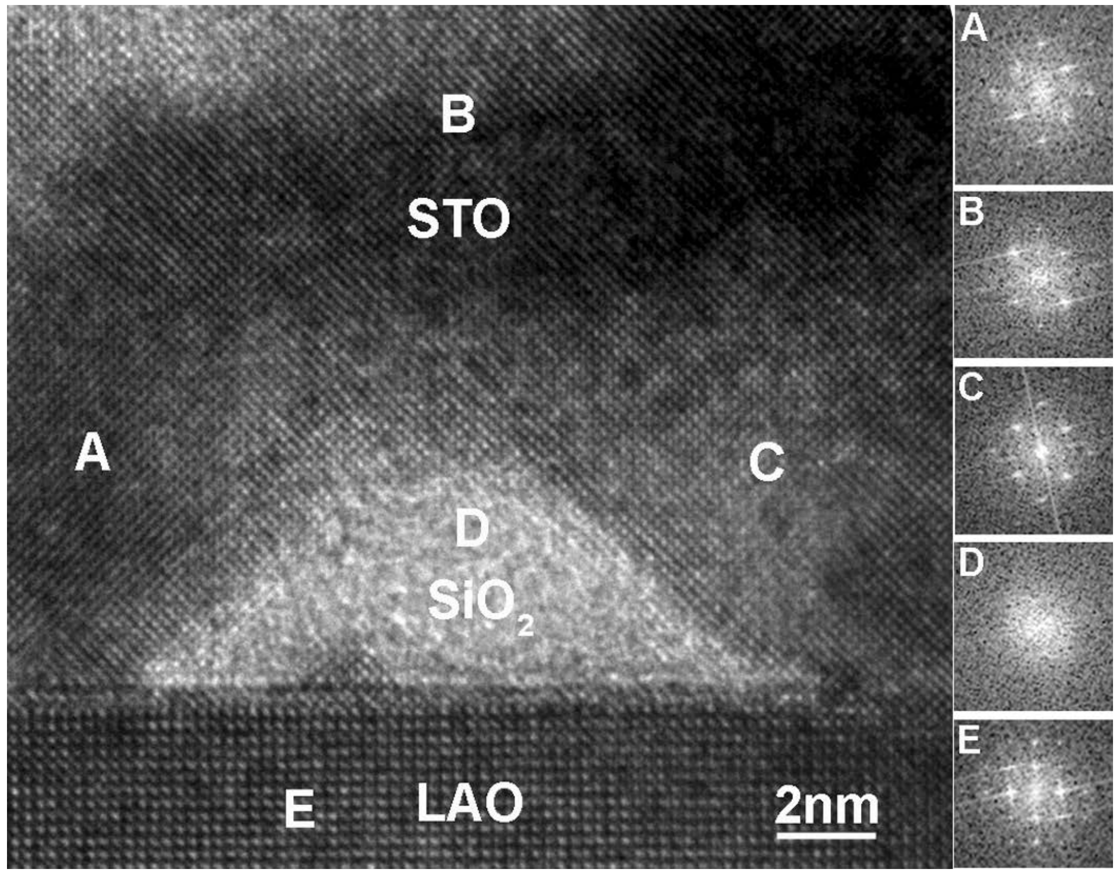
# Epitaxial Nanocomposite Films with Inclusion of Amorphous Nanoparticles



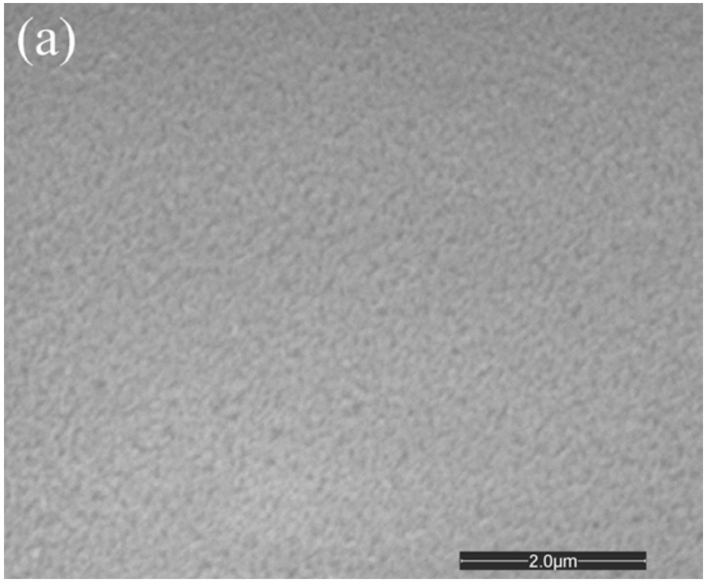

**Vertical:**
**hetero-epitaxial growth**

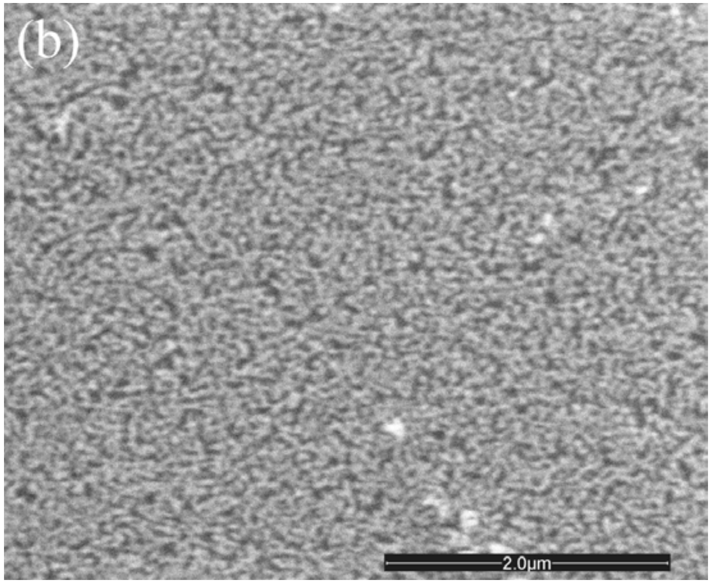
**Lateral:**
**homo- epitaxial growth**




*Angew. Chemie. Int. Ed.* **47**, 5768 (2008).

# Porous Epitaxial Films by Etching off $SiO_2$ Nanoparticles

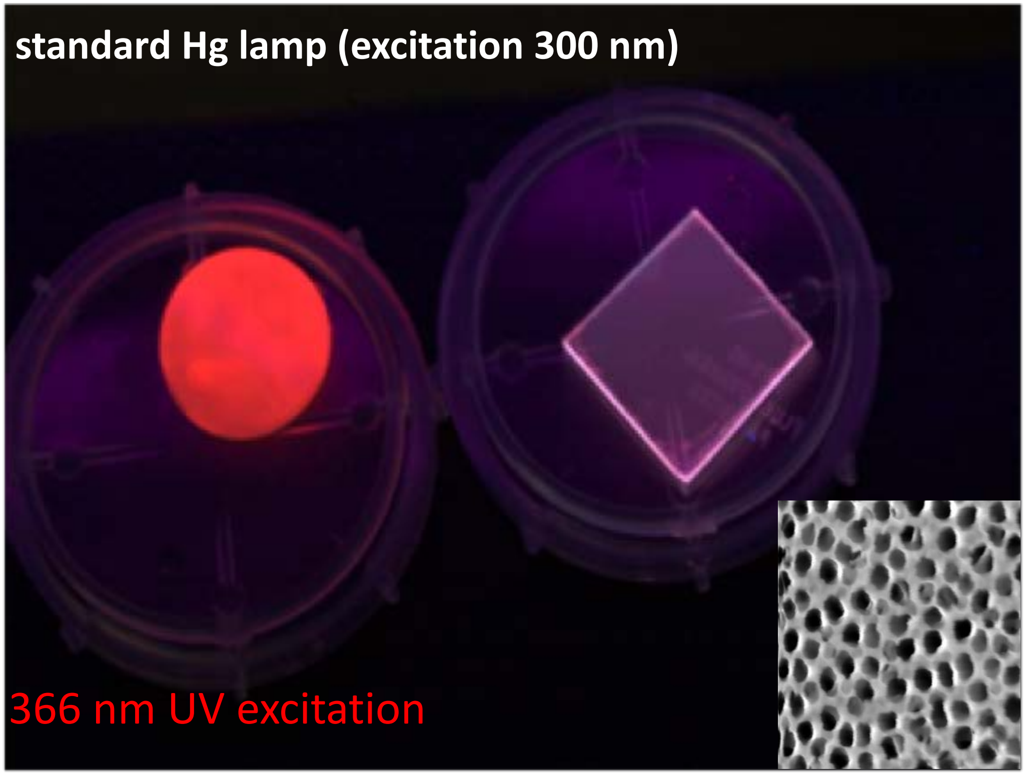


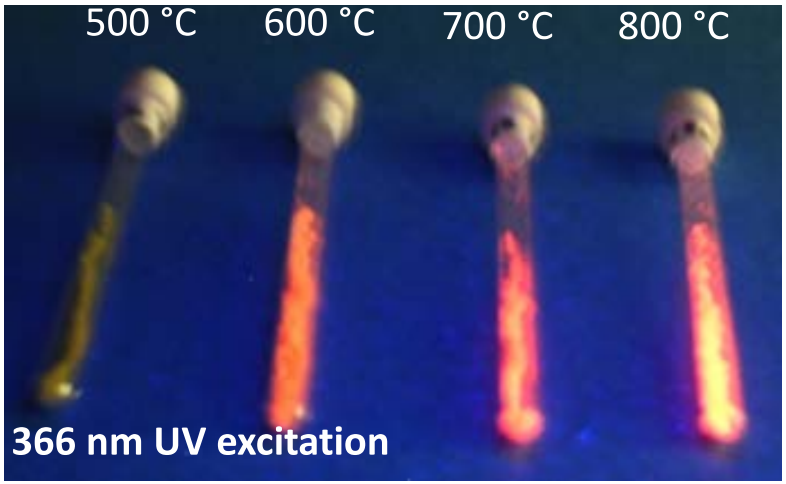

**As-deposited composite**

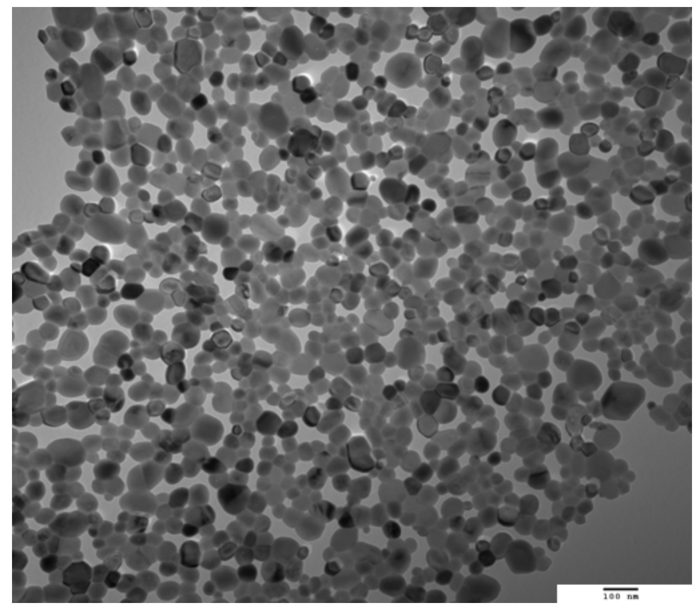
**After etching off $SiO_2$**

# PAD Application: Coating Phosphors on Nanostructures for Improved Light Output



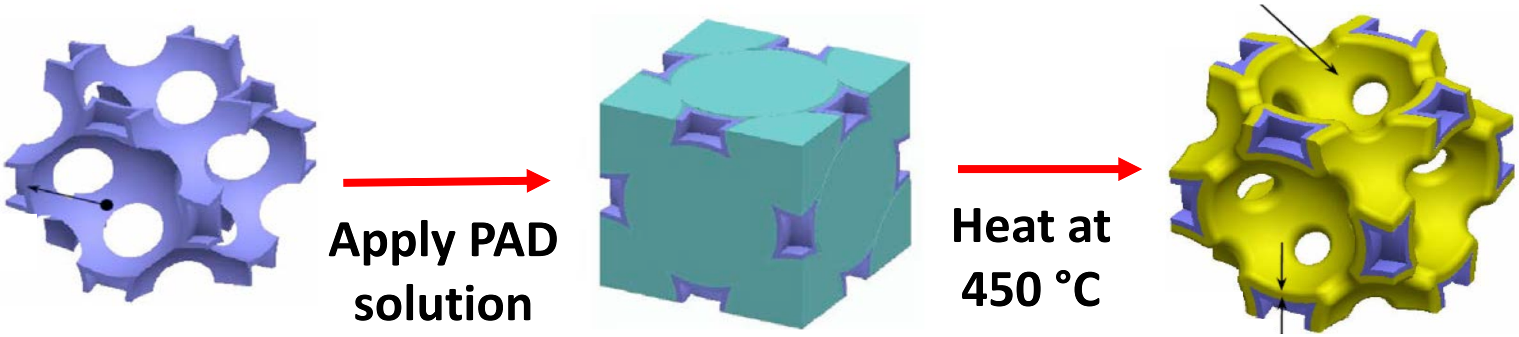
# PAD Application: Synthesis of Eu:$YVO_4$ Nanoparticle Networks

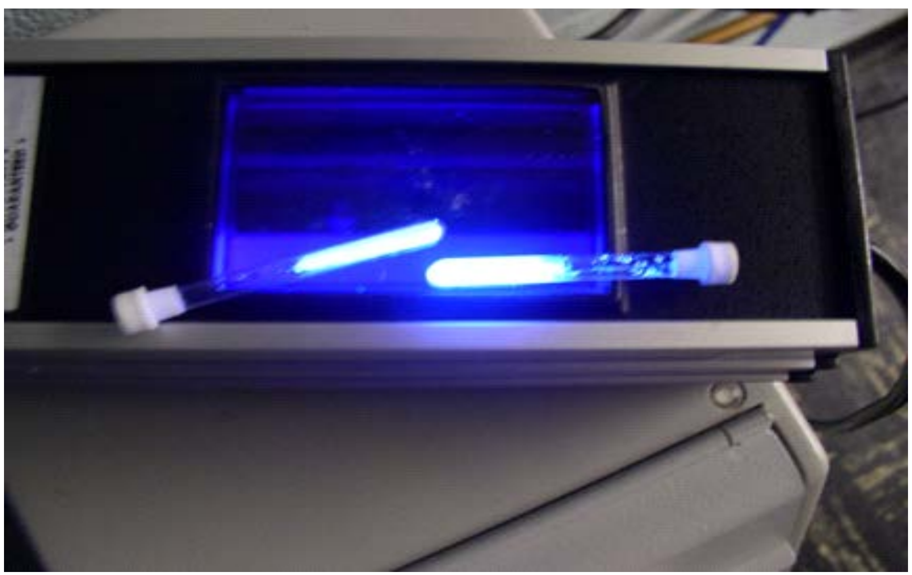


**Nanoparticle networks without aggregation**

# PAD Application: Coating Inverse Opals to Achieve a New Class of Scintillating Materials



**Hf coated inverse opals photographed in room light excited with a UV lamp.**

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# Challenges

- ☞Thick (> 1μm) films
- ☞Ultra thin (< 10 nm) films
- ☞Temperature used to de-polymerize the polymers
- ☞Carbon related issues

# Summary

- PAD is a new and powerful coating technique to synthesize electronic materials with desired structural and physical properties.

- PAD has no limit to size and shape of objects coated and has broad applications in different fields.